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Quantitative local structure refinement from XANES: multi-dimensional interpolation approach

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A new method to determine local structure in terms of a few structural parameters is proposed and realised in *FitIt* software. It is based on fitting of X-ray absorption near-edge structure (XANES) spectra using the combination of full multiple-scattering calculations, and multi-dimensional interpolation of spectra as a function of structural parameters. The procedure is divided into two steps: the construction of an interpolation polynomial, and the fitting of experimental spectra using the interpolation polynomial. During the construction of the polynomial, multiple-scattering calculations for certain sets of structural parameters are needed. The strategy for the selection of the most important expansion terms and corresponding sets of structural parameters is proposed. Fitting of the spectrum using multi-dimensional interpolation is very fast (a few seconds) because multiple-scattering calculations are unnecessary during this step. Also, this approach allows the development of a visual interface with the possibility of seeing the spectrum that corresponds to any set of structural parameters immediately. Thus, using a very limited number of multiple-scattering calculations, which are most time-consuming, it is possible to fit XANES. The interpolation polynomial construction procedure for three model molecules, FeS_4, FeO_6 and $Ni(CN)_4$, is demonstrated. An additional test has been performed for the latter most-complex example to check the assumption that a minimum of discrepancy between theoretical and experimental spectra corresponds only to the correct structure of the complex. A comparison with another XANES fitting software, *MXAN*, is given.

Keywords: XANES; X-ray absorption; fitting; *FitIt*; *MXAN*.

1. Introduction

Nowadays it is well known that an X-ray absorption spectrum is very sensitive to the local structure around the absorbing atom. In particular, extended X-ray absorption fine-structure (EXAFS) analysis is successfully used to determine bond lengths, coordination numbers and type of nearest neighbours of the absorbing atom. The extraction of structural information from X-ray absorption near-edge spectra is more complex because of the effects of multiple scattering of the photoelectron in this region of the spectra, and therefore there is no direct way to extract structural information from an experimental spectrum (like Fourier transformation in EXAFS). On the other hand, multiple-scattering (MS) effects in the XANES lead to a sensitivity of the spectrum to the bond angles. The mean free path of the photoelectron is also longer in the XANES region (Muller *et al.*, 1982). Thus the spectrum is rather sensitive to the positions of the atoms, which are at a distance of up to 4–5 Å from the absorbing atom.

A few approaches are currently being developed to extract quantitative structural information from XANES. Two of them come from EXAFS analysis. It was proposed (Bugaev *et al.*, 2001) to use Fourier filtration of XANES to determine the interatomic distances and coordination numbers. This technique allows obtaining the same structural information as in classical EXAFS, but can be applied in those cases when the spectra are measured over a very limited k-range. However, the possibility of extracting single-scattering contributions from XANES has been demonstrated only for crystalline compounds and minerals consisting of low-Z elements (Bugaev *et al.*, 1998, 2000). For other materials the perspectives of this methodology are still unknown.

The second technique, which uses the XANES region of spectra in a way close to EXAFS analysis, is fitting of XAS in the k-range starting from $k = 0$ and taking into account the limited number of MS paths. Most of the modern EXAFS fitting codes [*FEFFIT* (Newville *et al.*, 1995; Newville, 2001), *EXCURVE* (Gurman *et al.*, 1986), *GNXAS* (Filipponi *et al.*, 1995), *XFIT* (Ellis & Freeman, 1995)] allow the addition of MS paths during EXAFS analysis. Nevertheless, to the best of our knowledge a few attempts to start fitting from $k = 0$ were made only using the *XFit* code (Rich *et al.*, 1999; Weder *et al.*, 2001; Zhou *et al.*, 2003). Such a technique allows obtaining not only bond lengths and coordination numbers but also bond

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angles. The use of a limited number of MS paths in many cases does not allow the correct interpretation of the XANES regions and therefore can lead to the errors in the structure determination. The influence of the XANES region was significantly minimized using k^3 weighting of the spectrum during fitting and therefore not all of the structural information contained in XANES was extracted.

Full MS algorithms allow one to obtain accurately the XANES spectrum corresponding to a given geometry, but they are rather time-consuming. Thus the fitting of the spectra using these algorithms is a much more difficult procedure. A combination of full MS calculations and different methods of structure optimization (for example, molecular dynamics) can be used to probe the local structure (Smolentsev *et al.*, 2004), but from a spectroscopic point of view this technique is qualitative because it allows the most realistic geometrical model to be selected. However, the values of the structural parameters come from molecular dynamics and therefore the spectrum can be insensitive to certain parameters, or rather small variations of any parameter, which can lead to a better agreement between theoretical and experimental spectra.

Recently, a new method of extracting quantitative geometrical information by varying the structure and fitting XANES has been proposed (Benfatto & Della Longa, 2001). It has been applied to the local structure determination of the active metal site of the protein myoglobin (Della Longa *et al.*, 2001; Benfatto *et al.*, 2003), the zinc site of the protein superoxide dismutase (Benfatto *et al.*, 2001), and Co, Ni, Zn and Cu aqueous solutions (Angelo *et al.*, 2002; Benfatto *et al.*, 2002). This technique is based on a direct comparison of the experimental XAFS spectrum with the results of MS calculations for different sets of structural parameters. Such an approach has been realised in the *MXAN* computational procedure. It combines a MS scheme for calculations of XANES [namely the *CONTINUUM* code (Natoli & Benfatto, 1986)] and the multi-dimensional minima search functions *MINUIT* of the CERN library (James, 1994). For each set of structural parameters during the search of the minima the procedure of MS calculations is executed. Calculations of each spectrum are rather long (a few hours for disordered systems), and therefore the *MXAN* fitting procedure for a large number of parameters and for disordered systems is possible only using long workstation runs or clusters of high-performance computers.

In this paper we describe a new approach, which is realised in our *FitIt* computer program. It is based on the idea that it is possible to calculate the XANES spectrum for a set of geometrical parameters rather close to the initial one by expanding a spectrum as a function of several structural parameters. Within this assumption a fitting of structural parameters to minimize the discrepancy between theoretical and experimental spectra is a very fast procedure. This algorithm allows the significant reduction of the number of MS calculations and thus decreases the overall computational time. We will show for several models that by using a special polynomial interpolation scheme it is possible to obtain a very close fit of the interpolated XANES spectrum to the spectrum calculated by the *ab initio* approach, for any arbitrary set of structural parameters from physically limited intervals. Thus, if the *ab initio* theoretical XANES spectrum for the actual set of structural parameters reproduces the experimental spectrum, it will be possible using our approach to fit the real set of structural parameters by performing *ab initio* calculations only for a limited number of 'node' sets of structural parameters.

2. Method of calculation

2.1. Method of structure determination

It is well known that XANES is very sensitive to different conformational changes: structural distortions, exchange of atomic species, addition or loss of ligands, oxidation or reduction of absorbing atoms *etc.* To determine the structure of a compound under study in any unknown form (for example, after such modifications) it is necessary to construct an initial structural model which is rather close to the expected structure and to select the parameters of geometry which will be varied. All conformational changes have to be taken into account during construction of the initial model. Then bond lengths and angles can be refined by varying them within rather small physical limits (for example, for distances a typical value for such variation is about ±0.1 Å). For the refinement of these structural parameters the approach described below can be used.

To fit an XANES spectrum in the space of structural parameters we first construct an energy-dependent interpolation polynomial which reproduces a theoretical spectrum for all values of parameters within certain limits. *Ab initio* calculations of X-ray absorption spectra for different sets of parameters are performed at this stage. We suppose that an algorithm of spectra calculations is suitable for quantitative analysis of XANES and that the values of non-structural parameters have optimal values. To set these parameters correctly we propose to test the method using model compounds rather close to the studied ones, but with known structure. After minimization of the discrepancy between the theoretical and experiment spectra by varying the non-structural parameters, they should be fixed to exclude their influence on the results of local structure refinement.

All the *ab initio* calculations described below were performed using the *FEFF*8.2 package (Ankudinov *et al.*, 1998) with the following non-structural parameters: Hedin–Lunqvist exchange potential, with additional imaginary part 1.0 eV (typical experimental broadening), self-consistent calculations of potential with 15% overlapping of muffin-tin spheres and full MS calculations of spectra for the whole molecule. Self-consistent potential and phase shifts were calculated for each molecule and were then used as fixed during all subsequent calculations.

After polynomial construction (details of this procedure will be described below) we searched the minima of discrepancy between the experimental and interpolated spectra by varying the structural parameters. Here we assume that the values of the parameters, which correspond to the minimal discrepancy between the experimental and theoretical spectra (which we will call the best-fit parameters), are the closest to the values in the real system. In some cases it is possible that a few distinct best-fit structures exist. In such cases it is necessary to use additional spectral information [for example, to extend the analyzed energy ranges, to improve statistics on the experimental spectrum or to use additional XANES spectra (other absorption edges) of the same compounds] or to use arguments that come from other techniques. Multi-dimensional interpolation is very fast and therefore optimization of the strategy of multi-dimensional minima search is not very important. We use a simple gradient search of a minima algorithm. To find all local multi-dimensional minima we repeat this procedure starting from different random points. To compare interpolated and experimental spectra we use two standard criteria:

(i) the mean square deviation,

$$\frac{1}{E_2 - E_1}\int_{E_1}^{E_2}\left[\mu_{\rm i}(E) - \mu_{\rm exp}(E)\right]^2 {\rm d}E;$$

or (ii) the Chebishev criterion,

$$\max_{E_1 < E < E_2}\left|\mu_{\rm i}(E) - \mu_{\rm exp}(E)\right|,$$

where E_1 and E_2 are the energy limits of the spectra comparison, $\mu_{\rm i}(E)$ is the interpolated spectrum and $\mu_{\rm exp}(E)$ is the experimental spectrum. The same normalization of all spectra was used, $[1/(E_2 - E_1)]\int_{E_1}^{E_2}\mu^2(E)\,{\rm d}E = 1$.

Software realizing this fitting algorithm has been developed. It is called *FitIt* and has a visual user-friendly interface. The configuration of the program to be used in combination with different MS codes [currently *FEFF* (Ankudinov *et al.*, 1998), *G4XANES* (Della Longa *et al.*, 1995) and *FDMNES* (Joly, 2001)] is possible.

2.2. Multi-dimensional interpolation approximation

As mentioned above, the most time-consuming part of the XANES fitting procedure is MS calculations of spectra. Therefore the minimization of the number of required spectra calculations is essentially important. For this purpose we propose to use multi-dimensional interpolation of the spectrum as a function of the structural parameters. This means that to calculate the absorption coefficient $\mu(E)$ for the set of parameters $\mathbf{p}' = (p_1 + \delta p_1, p_2 + \delta p_2, \ldots, p_n + \delta p_n)$, where $\mathbf{p}^0 = (p_1, p_2, \ldots, p_n)$ is a starting set of structural parameters and δp_n is a deviation of parameter p_n from the starting value, we use the following expansion,

$$\begin{aligned}\mu_{\rm i}\big(E, p_1 + \delta p_1, p_2 + \delta p_2, \ldots, p_n + \delta p_n\big) &= \mu(E, p_1, p_2, \ldots, p_n) + \sum_n A_n(E)\delta p_n \\ &\quad + \sum_{m,n} B_{mn}(E)\delta p_m \delta p_n + \ldots. \end{aligned} \qquad (1)$$

The main problem in this case is to calculate energy-dependent coefficients and to find a minimal number of terms which are necessary to interpolate the spectrum correctly. The coefficients can be deduced from the results of MS calculations for certain sets of structural parameters solving a linear system of equations,

$$\mu_{\rm i}\big(E, \mathbf{p}^k\big) = \mu\big(E, \mathbf{p}^k\big). \qquad (2)$$

In this formula, $\mathbf{p}^k$ is the set of structural parameters for the interpolation node number k, $\mu(E, \mathbf{p}^k)$ is the result of MS calculations of the XANES spectrum for this set of parameters, and $\mu_{\rm i}(E, \mathbf{p}^k)$ is the interpolated spectrum calculated using (1), which contains a linear combination of unknown coefficients $A_n(E), B_{mn}(E)$. The set of parameters $\mathbf{p}^k$ in the aggregate with corresponding spectrum $\mu(E, \mathbf{p}^k)$, which is exactly equal to an interpolated spectrum, we will call the 'interpolation node'. If, from the symmetry of the molecule, it is clear that for different sets of parameters spectra are equal, corresponding interpolation nodes will be called equivalent. In the simplest case of the linear interpolation of a spectrum with one structural parameter, the interpolated spectrum becomes just a linear combination of two spectra,

$$\mu_{\rm i}\big(E, p^0 + \delta p\big) = \mu\big(E, p^0\big) + \frac{\mu\big(E, p^1\big) - \mu\big(E, p^0\big)}{p^1 - p^0}\,\delta p.$$

2.3. Construction of the polynomial

The number of terms necessary to interpolate an XANES spectrum correctly depends on the particular system, parameters and limits of variations. Therefore there is no universal interpolation polynomial, and a clear strategy of its construction is necessary. In Appendix *A* we have described the most important steps of this procedure. The proposed strategy consists of step-by-step testing and correction of the polynomial. Starting with the simplest polynomial, discrepancies between interpolated and MS-calculated spectra are checked for certain sets of structural parameters, which we will call 'control points'. They are selected so that the influence of the tested term of the polynomial is maximal for this set of parameters. For example, if one starts first with a linear approximation and wants to check the δp_1^2 term necessity, the control point $\delta p_1 = 0.5$, $\delta p_i = 0$ $(i = 2 \ldots n)$ must be used (here n is the total number of parameters). For $\delta p_1 \delta p_2$ the control point is $\delta p_1 = 1$, $\delta p_2 = 1$, $\delta p_i = 0$ $(i = 3 \ldots n)$ and for $\delta p_1 \delta p_2^2$ the control point is $\delta p_1 = 1$, $\delta p_2 = 0.5$, $\delta p_i = 0$ $(i = 3 \ldots n)$. Here and below, relative units for all deviations of parameters are employed ($\delta p_i = 0$ corresponds to the initial value of the parameter and $\delta p_i = 1$ corresponds to the deviation equal to the limit of the variation for this parameter). Also we will use vector notation for sets of parameters [for example, (1, 0.5) is equivalent to $\delta p_1 = 1$, $\delta p_2 = 0.5$].

If the modulus of the maximal discrepancy between interpolated and MS-calculated spectra exceeds 10% of the difference between MS calculations for the control set of parameters (control point) and the spectrum calculated for the initial set of the parameters [$\delta p_i = 0$ $(i = 1 \ldots n)$], then one has to include the corresponding term in the constructed interpolation polynomial. To calculate the energy-dependent coefficient for this term, a new equation corresponding to this control point is added into system (2). In the sequel this control point and corresponding spectrum form an interpolation node of the polynomial. The next control points are tested using this improved polynomial. If it is found that any term is negligible in the polynomial then it is possible to reduce the number of more complex terms, which have to be tested on subsequent steps, and thus reduce the number of control points that correspond with the required number of MS calculations.

There is good reason to believe that higher-order cross terms are negligible if they are the product of any previously neglected term and another one. It can be easily proved by contradiction in the case of systems without any symmetry. If our polynomial does not contain the term $\delta p_i \delta p_j$ but includes $\delta p_i \delta p_j \delta p_k$, it is clear that the expansion around different but rather close starting sets of parameters (for example, with different values of p_k) should be the same. Only energy-dependent coefficients should be different. Therefore the expansions for these two structures will not contain terms proportional to $\delta p_i \delta p_j$. On the other hand, the dependence on $\delta p_i \delta p_j$ will appear for the structure with changed value of p_k owing to the $\delta p_i \delta p_j \delta p_k$ term. This contradiction demonstrates an inexpediency of inclusion of considered higher-order terms. This rule is fundamental and it allows a convergence to be reached while constructing the interpolation polynomial very fast (see examples below).

For molecules with symmetry the situation is a bit different. The terms in expansion (1) should be invariant to symmetry operations. In many cases it allows odd terms from one parameter interpolation to be excluded (if positive and negative changes of parameter lead to the same spectrum changes), and the number of possible cross terms to be reduced. The analysis of cross terms, using the rule described above, sometimes leads to the loss of a few terms which describe the reduction of a symmetry, but an overall strategy based on this rule still remains fruitful. Therefore we propose to correct the polynomial constructed on the basis of this principle using symmetrically invariant terms, or terms corresponding to the highly asymmetric geometry.

3. Results and discussion

To demonstrate the validity of the multi-dimensional interpolation approximation and how the strategy described in Appendix *A* works, we have constructed interpolation polynomials for three types of coordination: tetrahedral, octahedral and square-planar. We suppose that the method will be very fruitful in the field of metallo-organic chemistry and especially for the investigations of active metal centres in the proteins. Therefore we have chosen arrangements which are common in this field: FeS_4, FeO_6 and $Ni(CN)_4$. The first two examples are very simple. Distances and angles were varied separately owing to the much smaller effect of the angles in comparison with the distance variations. The last example is more complex and demonstrates a typical procedure. Varied parameters are schematically shown in Fig. 1.

Table 1
Number of MS calculations and non-equivalent interpolation nodes needed to construct interpolation polynomials for model molecules.

Model	Varied parameters	Number of parameters	Number of MS calculations	Number of non-equivalent interpolation nodes
FeS_4	Distances	4	4	2
FeS_4	Angles	3	5	2
FeO_6	Distances	3	6	3
FeO_6	Angles	3	10	6
$Ni(CN)_4$	Distances and angles	6	32	15

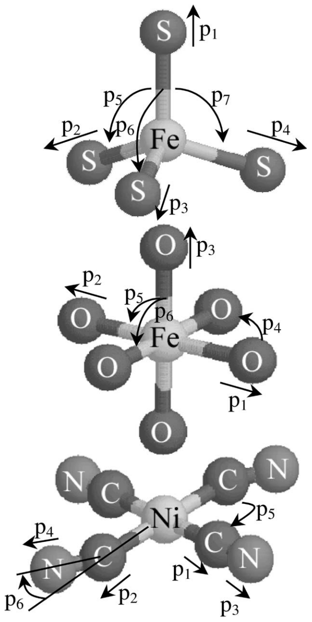

Figure 1
Pictorial view of the model molecules and varied structural parameters.

In Table 1 we have summarized a number of non-equivalent sets of structural parameters (control points) for which MS calculations were performed. Not all of these spectra were used as interpolation nodes. A part of them is calculated to show the unimportance of certain terms. The number of spectra which represent non-equivalent interpolation nodes is also listed.

In §3.2 we will check for $Ni(CN)_4$ that the assumption that the best-fit parameters found within the multi-dimensional interpolation approximation correspond to the unique 'correct' structure of the molecule, and discuss inaccuracies of the method. In the last section a comparison of the proposed approach with the algorithm realised in the *MXAN* software will be given.

3.1. Tests of approximation

3.1.1. Tetrahedral coordination. For the FeS_4 model structure with tetrahedral-type coordination, two types of structural parameters (Fe—S bond lengths and S—Fe—S angles) have been varied (seven structural parameters in total;

Table 2
List of non-equivalent control points used for MS calculations and all corresponding expansion terms of interpolation polynomials for the FeS_4 molecule. Terms are shown only for interpolation nodes. A few terms are associated with the same set of parameters if they are equivalent due to the molecule symmetry.

Step of strategy (see Appendix *A*)	Distances variation		Angles variation	
	Set of parameters	Terms of polynomial	Set of parameters	Terms of polynomial
2	(1, 0, 0, 0, 0, 0, 0)	δp_1, δp_2, δp_3, δp_4	(0, 0, 0, 0, 1, 0, 0)	δp_5, δp_6, δp_7
3	(1, 1, 0, 0, 0, 0, 0)		(0, 0, 0, 0, 1, 1, 0)	$\delta p_5 \delta p_6$, $\delta p_5 \delta p_7$, $\delta p_6 \delta p_7$
4	(0.5, 0, 0, 0, 0, 0, 0)	δp_1^2, δp_2^2, δp_3^2, δp_4^2	(0, 0, 0, 0, 0.5, 0, 0)	
6			(0, 0, 0, 0, 1, 1, 1)	

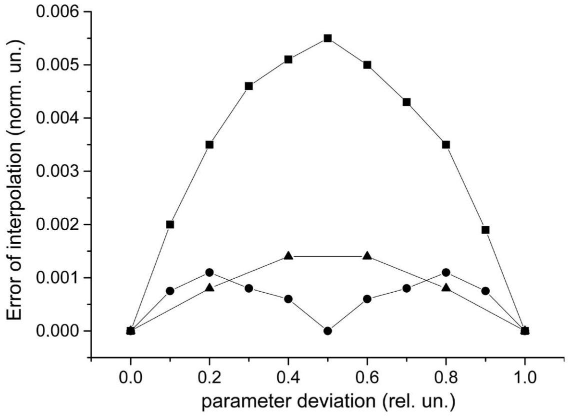

Figure 2
Maximal difference between interpolated and theoretical spectra for different values of the parameter deviation. Squares (triangles) correspond to first-order interpolation with the limit of variations being 0.2 (0.1) Å. Circles correspond to second-order interpolation with the limit of variations being 0.2 Å. Calculations were performed for Fe *K*-edge XANES of FeS_4 for variations of one of the bond lengths.

see Fig. 1). The limits of variations were 0.2 Å for distances (δp_1, δp_2, δp_3, δp_4) and 29° for angles (δp_5, δp_6, δp_7).

To demonstrate the accuracy of the method for different limits of variations we have presented in Fig. 2 the maximal error of interpolation as a function of deviation of one parameter (the Fe—S bond length). Dependencies for two limits of variations (0.1 and 0.2 Å) are shown. As can be clearly seen, the largest error value is in the centre between interpolation nodes (the nodes are $\delta p_1 = 0$ and $\delta p_1 = 1$ for first-order interpolation and $\delta p_1 = 0$, $\delta p_1 = 0.5$ and $\delta p_1 = 1$ for second-order interpolation), and it increases very fast with expansion of the variation limits. The maximal difference between the spectrum for the initial structure and that for another one corresponding to a 0.1 Å elongation of the Fe—S bond length is 0.02 normalized units. In the case of the first-order interpolation with 0.2 Å limit the error is 0.0055 normalized units (more than 25%) and therefore it is necessary to add a second-order term or reduce the limits of the variations. When the limit of variation is 0.1 Å the largest error is 15%. A more effective way of improving the interpolation is to add the second-order term. In this way the error of interpolation is again maximal almost in the middle between interpolation points ($\delta p_1 = 0.2$ and $\delta p_1 = 0.8$) and equal to 10% for $\delta p_1 = 0.2$ and 3% for $\delta p_1 = 0.8$. In some cases it is very important to reduce the error of one-parameter interpolation for the higher values of parameters, because the influence of cross terms increases in this region and the simultaneous influence of both these factors can lead to the incorrect interpolation. Therefore the possibility of reducing this error by adding a second-order term into the one-parameter interpolation is very important.

In the case of a tetrahedron the variation of angles leads to much smaller modifications of spectra in comparison with distances. Even with very large changes of angle (−30°) the maximal effect is four times smaller than the effect of a 0.2 Å distance elongation. Therefore there are three possibilities: to increase the limits of the variations of angles (but in this case the higher-order interpolation polynomial for the angles will be needed and therefore this variant is unfavourable); to reduce the limits of the distance variations; or to vary the distances and angles independently (firstly all the distances with fixed angles and then the angles with fixed best-fit parameters for the distances). Below we will demonstrate the latter variant with independent interpolation polynomials for distances and angles.

To construct the polynomials the strategy described in Appendix *A* was used. As a first approximation we have interpolated the spectrum linearly. For this purpose MS calculations for sets of parameters (1, 0, 0, 0, 0, 0, 0) and (0, 0, 0, 0, 1, 0, 0) were performed. Then we analyzed the importance of cross terms on the basis of the comparison of linearly interpolated and MS-calculated spectra for the sets of parameters (1, 1, 0, 0, 0, 0, 0) and (0, 0, 0, 0, 1, 1, 0). It was found that such terms are important only for angle variations (parameters p_5, p_6, p_7). Using the same polynomial we have tested the influence of square terms on the basis of spectral comparison for other sets of parameters: (0.5, 0, 0, 0, 0, 0, 0) and (0, 0, 0, 0, 0.5, 0, 0). We have concluded that such terms should be taken into account in the case of distances variations only. After improvement of the polynomial according to our strategy we have analyzed only one cross term with three parameters (for angular deviations only). Comparison of interpolated and MS-calculated spectra for the set of parameters (0, 0, 0, 0, 1, 1, 1) demonstrated that this term is negligible. These steps of polynomial construction are summarized in Table 2.

Thus we have obtained the following interpolation polynomials,

$$\mu_i = \mu(\mathbf{p}^0) + \sum_{n=1}^{4} A_n(E)\delta p_n + \sum_{n=1}^{4} B_n(E)\delta p_n^2$$

for distances, and

$$\mu_i = \mu(\mathbf{p}^0) + \sum_{n=5}^{7} A_n(E)\delta p_n + \sum_{\substack{n,m=5 \\ n \neq m}}^{7} B_{mn}(E)\delta p_m \delta p_n$$

for angles.

Table 3
List of non-equivalent control points used for MS calculations and all corresponding expansion terms of the interpolation polynomials for the FeO_6 molecule. Terms are shown only for interpolation nodes. A few terms are associated with the same set of parameters if they are equivalent due to the molecule symmetry.

	Distances variation		Angles variation	
Step of strategy	Set of parameters	Terms of polynomial	Set of parameters	Terms of polynomial
2	(1, 0, 0, 0, 0, 0)	δp_1, δp_2, δp_3	(0, 0, 0, 1, 0, 0)	δp_4^2, δp_5^2, δp_6^2
3	(1, 1, 0, 0, 0, 0) (1, 0, 1, 0, 0, 0)	$\delta p_1 \delta p_2$	(0, 0, 0, 1, 1, 0) (0, 0, 0, −1, 1, 0) (0, 0, 0, 0, 1, 1) (0, 0, 0, 0, −1, 1) (0, 0, 0, 1, 0, 1)	$\delta p_4^2 \delta p_5^2$ $\delta p_4 \delta p_5^2$ $\delta p_5^2 \delta p_6^2$ $\delta p_5 \delta p_6$
4	(0.5, 0, 0, 0, 0, 0)	δp_1^2, δp_2^2, δp_3^2	(0, 0, 0, 0.5, 0, 0)	δp_4^4, δp_5^4, δp_6^4
5	(1, 0.5, 0, 0, 0, 0)		(0, 0, 0, 1, 0.5, 0) (0, 0, 0, 0.5, 1, 0) (0, 0, 0, 0, 1, 0.5)	

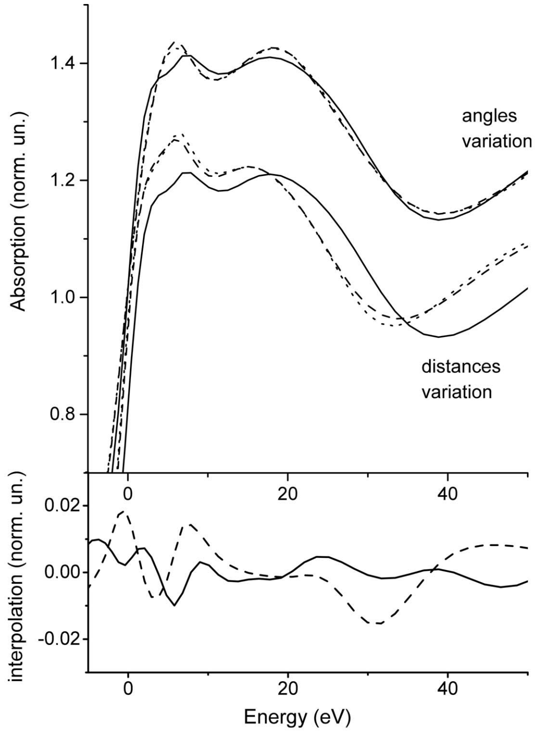

Figure 3
Top: comparison of interpolated (dots) and MS-calculated (dashes) spectra for control sets of parameters: (0.8, 0.8, 0.8, 0.8, 0, 0, 0) (all varied distances are equal to 2.46 Å) for distances variation and (0, 0, 0, 0, 0.8, 0.8, 0.8) (all varied angles are equal to 132°) for angles variation. Solid lines correspond to the MS calculations for the initial set of parameters (0, 0, 0, 0, 0, 0, 0). It is difficult to resolve the dotted and dashed curves because they are very close. Bottom: difference between interpolated and MS-calculated spectra for control sets of parameters. The solid (dashed) line corresponds to the angles (distances) variation. Calculations were performed for Fe *K*-edge XANES of FeS_4.

In Fig. 3 we have presented interpolated and calculated spectra for the set of parameters (0.8, 0.8, 0.8, 0.8, 0, 0, 0) and starting calculated spectrum. We have chosen this set of parameters because we expected maximal error of interpolation for them (one-parameter interpolation has a maximal error at this point, and cross terms, which were neglected, were also rather large because they increase with the increase of values of all parameters). The quality of interpolation during angle variations is demonstrated in Fig. 3 for an analogous set of parameters. As can be clearly seen, the interpolated spectrum reproduces all trends quite well and the error of interpolation is much less than the effect of parameters changes on the spectrum.

3.1.2. Octahedral coordination. In this case we have varied the following structural parameters: three Fe—O distances and three O—Fe—O angles. Schematically they are shown in Fig. 1. The limits of variations were 0.2 Å for distances (δp_1, δp_2, δp_3) and ±20° for angles (δp_4, δp_5, δp_6). In the case of octahedral geometry it was also reasonable to vary the distances and angles independently because distance variations influence mostly the relative energy positions of XANES features while angle variations influence mostly the intensity of the main peak.

Owing to the symmetry (positive and negative increments of parameters correspond to the same spectra), linear terms for angles variations are zeros. Therefore we used the following interpolation polynomial as a first approximation,

$$\mu_i = \mu(\mathbf{p}^0) + \sum_{1}^{3} A_i(E)\delta p_i$$

for distances and

$$\mu_i = \mu(\mathbf{p}^0) + \sum_{4}^{6} A_i(E)\delta p_i^2$$

for angles. Inclusion of additional interpolation nodes for single-parameter interpolations allows the error of interpolation to be minimized (see step 4 in Table 3).

Angular distortions between bonds in three perpendicular planes demonstrate different types of symmetry invariant cross terms. From the symmetry it is clear that spectra calculated for the sets of parameters (0, 0, 0, 1, 1, 0) and (0, 0, 0, 1, −1, 0) are exactly the same, but differ from the following couple of sets: (0, 0, 0, −1, 1, 0) and (0, 0, 0, −1, −1, 0). Term $\delta p_4 \delta p_5^2$ allows these symmetrical relations to be reproduced. A couple of parameters, p_5 and p_6, demonstrate another case: sets of parameters (0, 0, 0, 0, 1, 1) and (0, 0, 0, 0, −1, −1) are equivalent, but differ from the couples (0, 0, 0, 0, −1, 1) and (0, 0, 0, 0, 1, −1). Therefore cross term $\delta p_5 \delta p_6$ has to be considered. Simultaneous variations of parameters p_4 and p_6 do not lead to the loss of symmetry for each of these parameters; therefore cross term $\delta p_4^2 \delta p_6^2$ has to be used, but it is

Table 4
List of non-equivalent control points used for MS calculations and all corresponding expansion terms of interpolation polynomials for the FeO_6 molecule. Terms are shown only for interpolation nodes. A few terms are associated with the same set of parameters if they are equivalent due to the molecule symmetry.

Step of strategy	Set of parameters	Terms of polynomial
2	(1, 0, 0, 0, 0, 0)	$\delta p_{1,}\ \delta p_2$
	(0, 0, 1, 0, 0, 0)	δp_3, δp_4
	(0, 0, 0, 0, 1, 0)	δp_5^2
	(0, 0, 0, 0, 0, 1)	δp_6^2
3	(1, 1, 0, 0, 0, 0)	$\delta p_1 \delta p_2$
	(1, 0, 1, 0, 0, 0)	$\delta p_1 \delta p_3$, $\delta p_2 \delta p_4$
	(1, 0, 0, 1, 0, 0)	
	(1, 0, 0, 0, 1, 0)	$\delta p_1 \delta p_5^2$, $\delta p_2 \delta p_5^2$
	(1, 0, 0, 0, 0, 1)	
	(0, 1, 0, 0, 0, 1)	$\delta p_2 \delta p_6^2$
	(0, 0, 1, 1, 0, 0)	
	(0, 0, 1, 0, 1, 0)	
	(0, 0, 1, 0, 0, 1)	
	(0, 0, 0, 1, 0, 1)	$\delta p_4 \delta p_6^2$
	(0, 0, 0, 0, 1, 1)	
	(0, 1, 0, 1, 1, 1)	$\delta p_2 \delta p_4 \delta p_5 \delta p_6$
4	(0.5, 0, 0, 0, 0, 0)	δp_1^2, δp_2^2
	(0, 0, 0.5, 0, 0, 0)	δp_3^2, δp_4^2
	(0, 0, 0, 0, 0.5, 0)	$\delta {p_5}^4$
	(0, 0, 0, 0, 0, 0.5)	$\delta {p_6}^4$
5	(1, 0.5, 0, 0, 0, 0)	
	(1, 0, 0.5, 0, 0, 0)	
	(0.5, 0, 1, 0, 0, 0)	
	(1, 0, 0, 0, 0.5, 0)	
	(0.5, 0, 0, 0, 1, 0)	
	(0, 1, 0, 0, 0, 0.5)	
	(0, 0.5, 0, 0, 0, 1)	
	(0, 0, 0, 1, 0, 0.5)	
	(0, 0, 0, 0.5, 0, 1)	
6	(1, 1, 0, 0, 1, 0)	$\delta p_1 \delta p_2 \delta p_5^2$
	(0, 1, 0, 1, 0, 1)	

negligible in the present case. Contributions from other terms are weak (see a list of control points in Table 3).

The couples of parameters p_1, p_2 and p_1, p_3 represent two types of distance variations with angles of 90° and 180° between bonds. Cross terms are different for these two cases and only one of them has been included in the polynomial. All other terms are neglected according to the strategy. At the end we have obtained the following polynomials,

$$\mu_i = \mu(\mathbf{p}^0) + \sum_{n=1}^{3} A_n(E)\delta p_n + \sum_{n=1}^{3} B_n(E)\delta p_n^2 + C(E)\delta p_1 \delta p_2$$

for distances and

$$\mu_i = \mu(\mathbf{p}^0) + \sum_{n=4}^{6} A_n(E)\delta p_n^2 + \sum_{n=4}^{6} B_n(E)\delta p_n^4 + C_{45}(E)\delta p_4 \delta p_5^2$$
$$+ D_{45}(E)\delta p_4^2 \delta p_5^2 + C_{56}(E)\delta p_5 \delta p_6 + D_{56}(E)\delta p_5^2 \delta p_6^2$$

for angles. All steps of polynomial construction are summarized in Table 3.

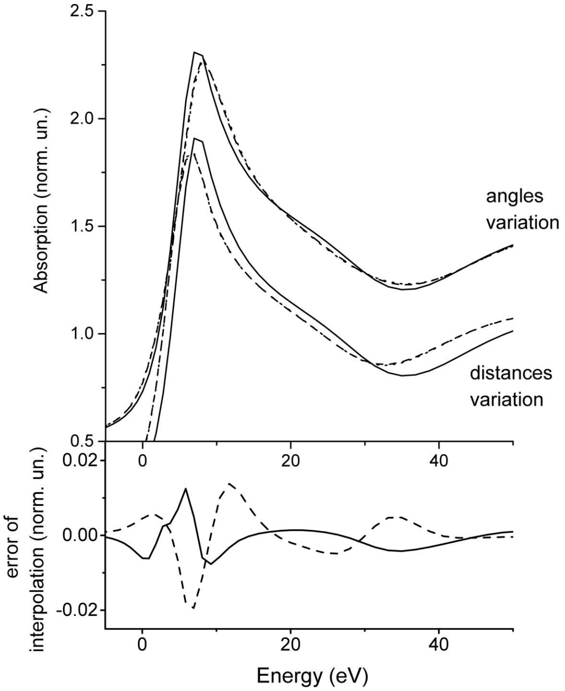

Figure 4
Top: comparison of interpolated (dots) and MS-calculated (dashes) spectra for control sets of parameters: (0.75, 0.75, 0.75, 0, 0, 0) for distances variation (all varied distances are equal to 2.15 Å) and (0, 0, 0, 0.75, 0.75, 0.75) for angles variation (all varied angles are equal to 105°). The solid lines correspond to the MS calculations for the initial set of parameters (0, 0, 0, 0, 0, 0). It is difficult to resolve the dotted and dashed curves because they are very close. Bottom: difference between interpolated and calculated spectra for control sets of parameters. The solid (dashed) line corresponds to the angles (distances) variation. Calculations were performed for Fe *K*-edge XANES of FeO_6.

To demonstrate how interpolation works we have presented in Fig. 4 calculated and interpolated spectra for the sets of parameters (0.75, 0,75, 0,75, 0, 0, 0) and (0, 0, 0, 0.75, 0.75, 0.75), for which we expect the maximal error of interpolation. For other sets of parameters the discrepancy between interpolation and MS calculations is smaller.

3.1.3. Square-planar coordination. The $Ni(CN)_4$ model molecule demonstrates a more complex example with six parameters varied simultaneously: parameters p_1 and p_2 represent first-shell distance changes while p_2 and p_3 represent second-shell distance variations. Parameter p_5 corresponds to the Ni—C—N angle deviation from 180° and parameter p_6 is the angle between the C—Ni—C chains (see Fig. 1). For all parameters the inversion symmetry was fixed. The following limits of variations were used: 0.2 Å for δp_1 and δp_2, 0.1 Å for δp_3 and δp_4 and 15° for δp_5 and δp_6.

In the same manner as for octahedral geometry only second-order terms have been considered as a first approximation for angular parameters. To achieve good one-parameter interpolation, additional interpolation nodes have been included (see step 4 in Table 4). It has been found that the cross terms between parameters, which are from perpendicular Ni—C—N chains, are negligible if at least one of these parameters perturbs only second-shell atoms (in particular $\delta p_1 \delta p_4$, $\delta p_1 \delta p_6^2$, $\delta p_3 \delta p_4$ *etc.*). This significantly reduced the number of subsequent control points during steps 5 and 6 (see the list of corresponding control points in Table 4). A reduc-

Table 5
Values of structural parameters p and unitless deviations δp for two distinct best-fit sets of parameters (Minimum 1 and Minimum 2), and 'correct' values which correspond to the MS-calculated spectrum used instead of the experiment during fitting.

	δp_1	p_1 (Å)	δp_2	p_2 (Å)	δp_3	p_3 (Å)	δp_4	p_4 (Å)	δp_5	p_5 (°)	δp_6	p_6 (°)
'Correct'	0.75	1.9	0.25	1.8	0.9	1.19	0.35	1.135	0.9	103.5	0.55	8.25
Minimum 1	0.19 (5)	1.788 (1)	0.87 (3)	1.924 (6)	0.38 (7)	1.138 (7)	1.00 (6)	1.200 (6)	1.04 (4)	105.6 (6)	0.2 (2)	3 (3)
Minimum 2	0.83 (3)	1.916 (6)	0.24 (2)	1.798 (4)	1.02 (6)	1.202 (6)	0.42 (7)	1.142 (7)	1.05 (5)	105.75 (75)	0.6 (2)	9 (3)

tion of symmetry during simultaneous variations of both angular parameters can be taken into account considering $\delta p_5 \delta p_6$ and $\delta p_5^2 \delta p_6^2$ terms [equivalent nodes are (0, 0, 0, 0, 1, 1) and (0, 0, 0, 0, −1, −1); (0, 0, 0, 0, 1, −1) and (0, 0, 0, 0, −1, 1)] or adding terms which correspond to the maximally distorted geometry: $\delta p_2 \delta p_4 \delta p_5 \delta p_6$ (in this case only positive values of angular deviations will be reasonable). Using this variant we have obtained the following interpolation function,

$$\begin{aligned}\mu_i = \mu(\mathbf{p}^0) &+ \sum_{n=1}^{4} A_n(E)\delta p_n + \sum_{n=1}^{6} B_n(E)\delta p_n^2 + \sum_{n=5}^{6} C_n(E)\delta p_n^4 \\ &+ D_{12}(E)\delta p_1 \delta p_2 + D_{13}(E)\delta p_1 \delta p_3 + D_{24}(E)\delta p_2 \delta p_4 \\ &+ E_{26}(E)\delta p_2 \delta p_6^2 + E_{46}(E)\delta p_4 \delta p_6^2 + E_{15}(E)\delta p_1 \delta p_5^2 \\ &+ E_{25}(E)\delta p_2 \delta p_5^2 + F_{125}(E)\delta p_1 \delta p_2 \delta p_5^2 \\ &+ G_{2456}(E)\delta p_2 \delta p_4 \delta p_5 \delta p_6.\end{aligned}$$

All steps of the polynomial construction are summarized in Table 4.

Calculated and interpolated spectra for the control set of structural parameters (0.75, 0.75, 0.75, 0.75, 0.75, 0.75) are shown in Fig. 5. Good agreement has been obtained.

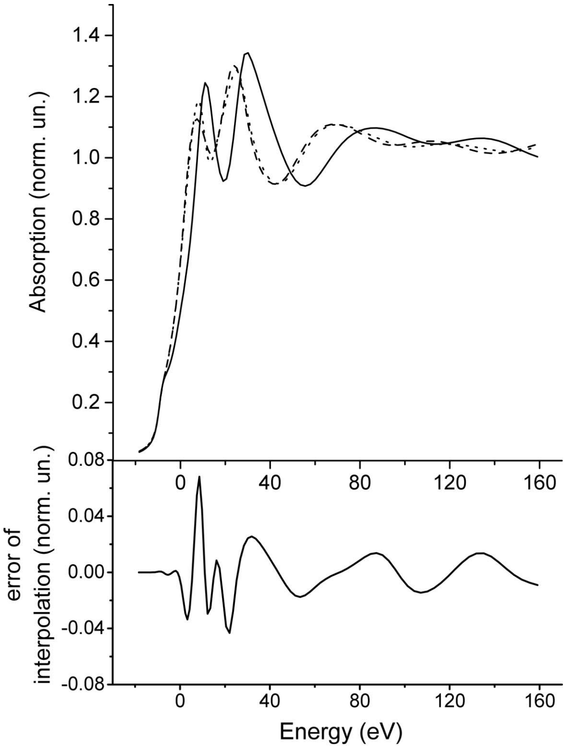

Figure 5
Top: comparison of interpolated (dotted) and MS-calculated (dashed) spectra for control sets of parameters: (0.75, 0.75, 0.75, 0.75, 0.75, 0.75) (Ni—C bond lengths are 1.9 Å, C—N bond lengths are 1.175 Å, angle between C—Ni—C chains is 101.25° and Ni—C—N angle is 168.75°). Solid lines correspond to the MS calculations for the initial set of parameters (0, 0, 0, 0, 0, 0). It is difficult to resolve the dotted and dashed curves because they are very close. Bottom: difference between interpolated and calculated spectra for control sets of parameters. Calculations were performed for Ni *K*-edge XANES of $Ni(CN)_4$.

3.2. Convergence of the fitting procedure

To demonstrate that the proposed interpolation approximation does not lead to serious errors in the determination of the structural parameters, and to check the assumption that the discrepancy between the theoretical and experimental spectrum is minimal for the correct values of the structural parameters, we have tested the convergence of the fitting procedure for the $Ni(CN)_4$ molecule. We have used the results of MS calculations for the random set of structural parameters, which we will call 'correct', instead of the experimental spectrum. Then we have started a fitting procedure to test if the best-fit parameters are close to these 'correct' parameters or not. For the $Ni(CN)_4$ model molecule we used structural parameters and the interpolation polynomial described above. To find all local minima, a gradient search in the space of the structural parameters was performed from 20 random points. Mean square deviation was minimized with precision 0.001 normalized units. We would like to stress that during this procedure it is not necessary to perform any MS calculations and therefore the minimization is very fast (a few seconds).

Two minima with the same discrepancy of 0.008 normalized units have been found. Best-fit parameters and 'correct' values are listed in Table 5 to demonstrate the different sensitivity of the spectrum to the parameters uncertainties, which corresponds to a 0.001 normalized unit increase of the discrepancy between the theoretical and experimental spectra. For real systems (and real experimental spectra) we expect the precision of the first-shell distances determination to be in the range 0.02–0.05 Å. Neglecting the p_6 parameter, two minima correspond to approximately the same geometry with another indexing of parameters. The deviation of the Ni—C—N angle (p_6) for one of the chains leads to non-equivalence of structures and thus an additional 'false' minimum appears. Two reasons leading to the appearance of this minimum are possible. It can be an error of interpolation and in this case the discrepancy between the interpolated and MS-calculated spectrum for this set of parameters should be significant. The alternative assumption that only the correct structure corresponds to the minimal discrepancy between the theoretical and experimental spectra can be invalid. Then experimental, interpolated and MS-calculated spectra should be very similar. As is clear from Fig. 6, the discrepancy between the experi-

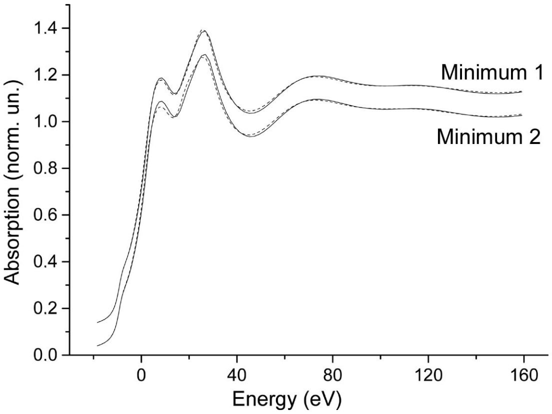

Figure 6
Results of MS calculations for two best-fit sets of parameters (dashes) and for the 'correct' structure (solid line). Values of structural parameters are listed in Table 5. Calculations were performed for Ni *K*-edge XANES of $Ni(CN)_4$.

mental and MS-calculated spectrum for the set of parameters 'Minimum 1' ('false' minimum) is very small. This means that the second reason described above is valid. We have to conclude that XANES spectra are very similar for two distinct structures and therefore in some cases it is impossible to obtain a unique set of structural parameters on the basis of XANES analysis alone (or at least it is necessary to increase the amount of spectroscopic information: analyzed energy range or resolution of spectra *etc.*). Nevertheless, we have quite a good sensitivity to the distance in Ni—C—N chains and these distances can be obtained rather accurately and uniquely from XANES analysis. Only the results for the angles do not have a single meaning, but they influence the distances rather weakly. In any case one of the best-fit sets of parameters is very close to the 'correct' values. For distance determination the error is 0.02 Å for an angle between chains of 2.5° and for a Ni—C—N angle of 6°. The errors do not exceed the typical sensitivity of the XANES spectra to these parameters and therefore the use of the multi-dimensional interpolation approximation does not lead to significant errors and thus the application of the method is reasonable.

3.3. Comparison with *MXAN*

As is clear from the examples described above, the multi-dimensional interpolation of XANES spectra as a function of the structural parameters allows XANES fitting to be performed on the basis of a very small number of MS calculations. This is the main advantage of the method because it leads to a significant reduction in overall computational time in comparison with the *MXAN* procedure (Benfatto & Della Longa, 2001), in which time-consuming MS calculations of the spectra need to be performed at each step of the minimum search. Nevertheless, our method requires additional analysis by the user to construct the interpolation polynomial. Therefore, a significant decrease in overall time (calculations of spectra and construction of polynomial) is expected mainly for complex cases (large clusters without symmetry) or using time-consuming algorithms of spectra calculations, such as the finite-difference method (Joly, 2001) which is very important for materials where the muffin-tin approximation for the potential is not valid. For simple compounds it is possible that by using the *MXAN* approach one can obtain a result faster. The limitation of the present method itself is that maximal values of the variations of the parameter have not to be too large. This is because it will be rather difficult to construct an interpolation polynomial if more than two terms are used for one-parameter interpolation. In many cases this internal limit of our *FitIt* software is close to the physical limits of parameter variations and therefore multi-dimensional interpolation can be used. The *MXAN* procedure is free from any limits except physical ones and from this point of view it is more universal.

The fitting procedure using *MXAN* for certain sets of non-structural parameters is fully automatic, but cannot be controlled by the user. It works perfectly when the values of non-structural parameters are correct. Otherwise the best-fit geometry can be unphysical because the effect of structural parameters on the XANES spectrum will compensate systematic errors arising from incorrect non-structural parameters. To avoid this, authors of *MXAN* propose to use an iterative strategy for the variations of structural and non-structural parameters. Our method requires the analysis of spectrum dependencies on structural parameters during polynomial construction and therefore it is less automatic. But the use of multi-dimensional interpolation allows the development of a visual interface for *FitIt.* Calculations of the spectra within this approach are very fast and can be performed in real time; therefore the user can immediately see the shape of the spectrum calculated for any set of structural parameters. Because of this, it is rather easy to identify the errors arising from incorrect values of non-structural parameters, and then set other criteria for experimental and theoretical spectra comparisons, which is insensitive to such uncertainties of non-structural parameters, or change the values of non-structural parameters. Here it is very important that for reasonable non-structural parameters only energy-dependent coefficients in the interpolation polynomial have to be recalculated. Therefore it is not necessary to repeat calculations for all control points which have not been included in the interpolation polynomial and repeat the full procedure of polynomial construction. Only the calculations for interpolation nodes are necessary. This allows the reduction of computational time during this step of the fitting.

The last advantage of the multi-dimensional interpolation approach realised in *FitIt* which we would like to mention is the separation of the interpolation polynomial construction and the fitting procedure. During the construction of the polynomial there is no comparison of the theoretical spectra with the experimental one. Only the discrepancies between interpolated and MS-calculated spectra are important. During the fitting procedure only the experimental and interpolated spectra are used and this step is very fast. Therefore it is possible to switch between different experimental spectra or different criteria of experimental and interpolated spectra comparisons without any additional MS calculations. It is useful, for example, to fit spectra of different phases of compounds which have a rather close structure or fit a series of spectra from time-resolved experiments. Using the algorithm, which is realised in *MXAN*, the sets of structural parameters for MS calculations depend on the discrepancy between theoretical and experimental spectra. Therefore the time-consuming procedure in *MXAN* has to be repeated for different experimental spectra or even other criteria of spectra comparison.

4. Conclusion

A novel approach for local atomic structure refinement on the base of theoretical XANES analysis is proposed. It is shown that, for different types of structural parameters within reasonable limits of variations, the multi-dimensional interpolation approximation is quite accurate and a rather small number of time-consuming MS calculations are needed to fit the XANES. We have demonstrated the method using examples typical for metallo-organic chemistry, but it can be applied to other compounds including crystals (we have already tested it, but these results are not presented here). A rather small number of MS calculations and visual control of the fitting procedures are the main advantages of the *FitIt* software.

APPENDIX *A*
Strategy of the polynomial construction

The strategy described below consists of the step-by-step testing and correction of the polynomial. It is based on the idea that higher-order cross terms are negligible if they are the product of any previously neglected term and another one, and on the criteria of the interpolation quality {the modulus of maximal discrepancy between interpolated and MS-calculated spectra is less than 10% of the difference between the MS calculations for the control point and the spectrum calculated for the initial set of parameters [$\delta p_i = 0 \ (i = 1 \ldots n)$]}. The logical sequence of steps of polynomial construction is shown in Fig. 7.

Step 1 is the choice of variation limits for the structural parameters. The influence of different parameters on the spectrum should be of the same order. If the influence of one parameter p_i is significantly less than another parameter p_j, a relative accuracy of interpolation as a function of p_j should be much smaller (and will require more terms in the interpolation polynomial). Otherwise the absolute error of interpolation for the parameter p_j will be comparable with the effect from variations of p_i. It is also reasonable to use not more than three nodes for single-parameter interpolation (it can be controlled in step 4). Otherwise there is a risk of having too many cross terms of high order. In the case of metal XANES spectra of metallo-organic compounds, a starting point for these limits can be 0.15–0.2 Å for the distances and 15–30° for the angles.

Step 2 is the choice of the first approximation for the interpolation polynomial. The simplest approximation is linear interpolation of spectra as a function of all parameters. To calculate derivatives in this case it is necessary to calculate spectra with only one parameter p_i maximally deviated from the starting values: $\delta p_i = 1$, $\delta p_j = 0$, $j = 1 \ldots n$, $j \neq i$. In some cases, from the symmetry of the cluster it is clear that positive and negative changes of a parameter will lead to the same effect on the spectrum (for example, parameter p_5 in the FeO_6 model molecule in Fig. 1). For such a parameter a linear term is equal to zero and thus one needs to use a second order in the polynomial.

Step 3 is the determination of cross terms with two parameters (p_i and p_k). For this purpose it is necessary to perform MS calculations for the following set of parameters: $\delta p_i = 1$, $\delta p_k = 1$, $\delta p_j = 0$, $j = 1 \ldots n$, $j \neq i, j \neq k$. If the error of interpolation is rather large (according to the criteria formulated above), this set of parameters and corresponding spectrum should be added as interpolation node. If there is almost no cross term influence on the result of the interpolation, higher-order terms with this couple of parameters and any other parameters can be negligible.

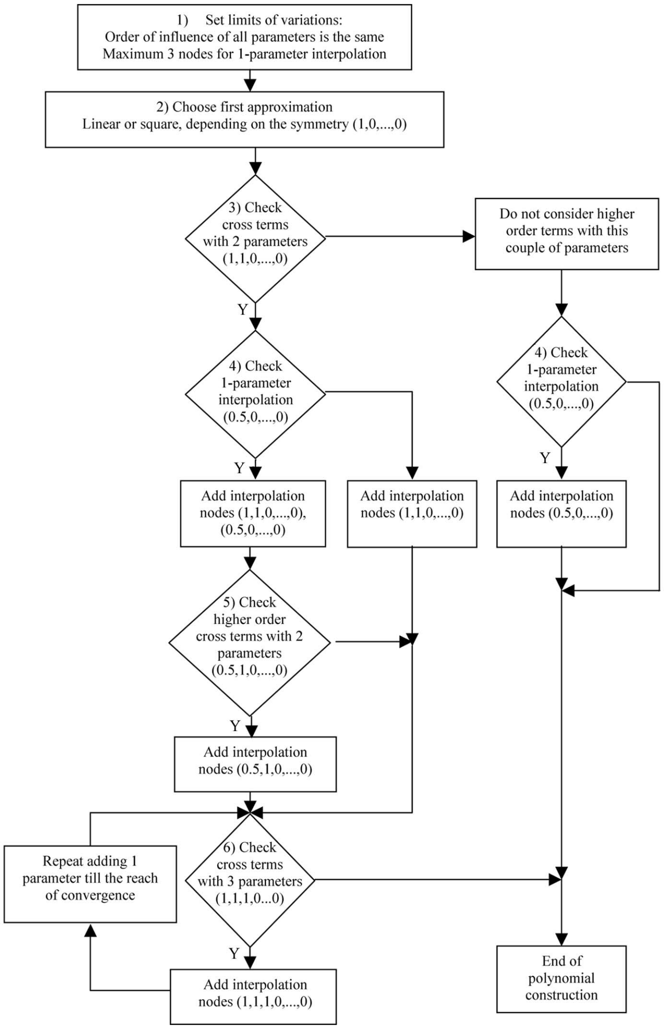

Figure 7
Logical sketch of the polynomial construction strategy. The numbers of steps and examples of control points are shown in corresponding blocks.

It can be that one parameter has symmetry (for example, parameter p_4 for the FeO_6 model molecule in Fig. 1) and thus we ignore its linear term and add its second-order term, but after changes of another parameter (for example, parameter p_5 for the FeO_6 model molecule in Fig. 1) this symmetry has been lost. It is reasonable in this case to use a term which is invariant to the symmetry operations (for example, term $\delta p_4 \delta p_5^2$ for the FeO_6 model molecule). Also, in most of the cases the same results can be obtained by adding to the initial polynomial a term corresponding to highly asymmetric geometry [for example, term $\delta p_2 \delta p_4 \delta p_5 \delta p_6$ for the $Ni(CN)_4$ model molecule].

Step 4 is the comparison of the results of the interpolation as a function of each variable and MS calculations. Maximal deviation of the interpolated spectrum from calculations using MS theory is expected for the following sets of the parameters: $\delta p_i = 0.5, \delta p_j = 0, j = 1 \ldots n, j \neq i$ (see Fig. 2), *i.e.* in the middle of the interval between interpolation nodes. Therefore these points should be used to control the accuracy of the interpolation. If the quality of interpolation is not sufficiently good it is necessary to add a higher-order term for this parameter (normally δp_i^2 is used, but for the parameters with symmetry effect, mentioned above, δp_i^4 is necessary).

Step 5 is the determination of higher-order cross terms with two parameters. Such analysis should be performed only for the couples of parameters with cross term included in step 3 and additional one-parameter terms included in step 4. The following control points have to be used: $\delta p_i = 1$, $\delta p_k = 0.5$, $\delta p_j = 0, j = 1 \ldots n, j \neq i, j \neq k$. In the case of a linear first approximation the corresponding terms are $\delta p_i \delta p_k^2$. For the second-order first approximation they are $\delta p_i^2 \delta p_k^4$.

Step 6 is checking of the cross terms with three parameters. This analysis should be performed only for the couples of parameters which contain the same parameters. For example, if one uses three cross terms: $\delta p_i \delta p_j^2$, $\delta p_j^2 \delta p_k$ and $\delta p_i \delta p_k$, one should consider only a single term: $\delta p_i \delta p_j^2 \delta p_k$. Owing to this and to the fact that normally not all of the cross terms between two variables are necessary, the number of subsequent terms (and therefore necessary MS calculations) decreases very rapidly. Analogous checks and improvements of the polynomial have to be performed until the convergence is reached (there is no possibility of constructing higher-order terms within the above-described limitations). For real compounds it can be reached rather fast.

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