

FitIt

Construction of interpolation polynomial

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The principal part of the XANES fitting procedure is construction of multidimensional interpolation polynomial. The number of terms, which are necessary to interpolate a XANES spectrum correctly, depends on the particular system, chosen parameters and limits of their variations. Therefore there is no universal interpolation polynomial, and a clear strategy of its construction is necessary. Bellow we will summarize the most important aspects of this procedure and then will give step-by-step description.

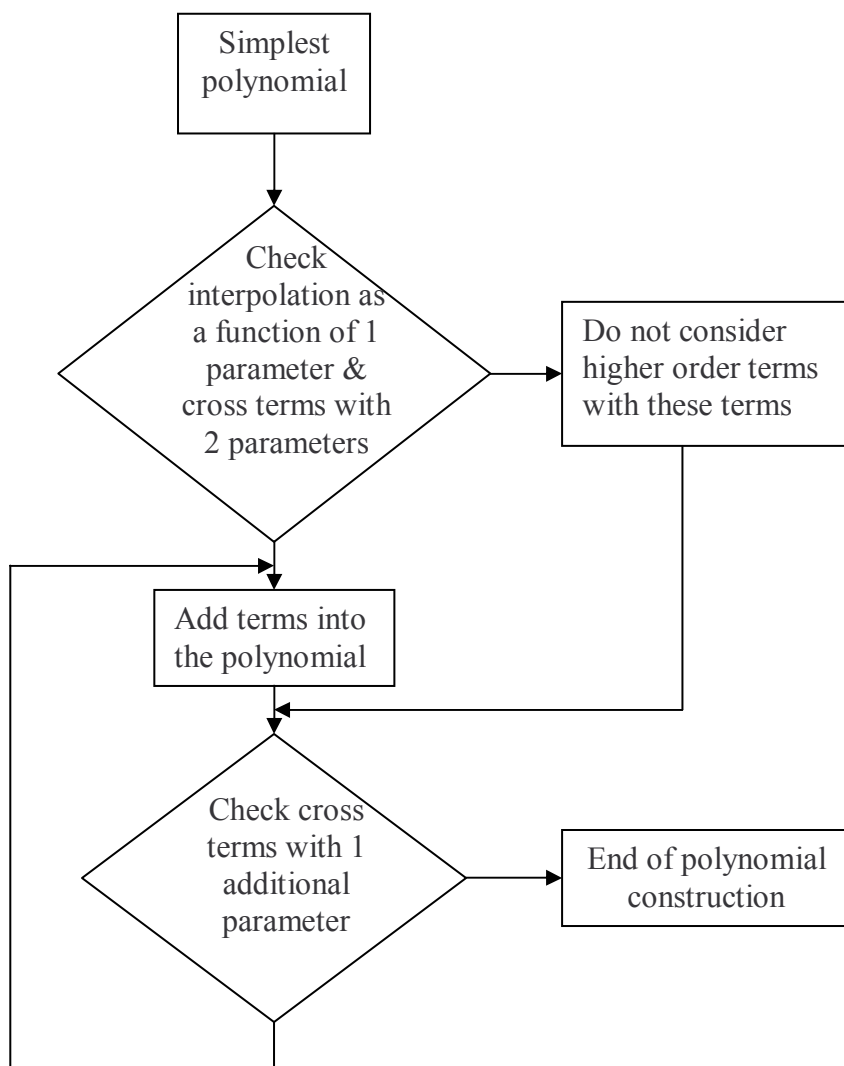


Fig. 1. General strategy of polynomial construction

The proposed strategy consists of step-by-step testing and correction of the polynomial schematically it is shown in Fig 1. Starting with simplest polynomial, discrepancies between interpolated and MS calculated spectra are checked for certain sets of structural parameters, which will be called “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 linear approximation and wants to check the δp_1^2 term necessity - control point $\delta p_1=0.5$, $\delta p_i=0$ ($i=2\dots n$) must be used (here n is a total number of parameters). For $\delta p_1\delta p_2$ control point is $\delta p_1=1$, $\delta p_2=1$, $\delta p_i=0$ ($i=3\dots n$) and for $\delta p_1\delta p_2^2$ control point is $\delta p_1=1$, $\delta p_2=0.5$, $\delta p_i=0$ ($i=3\dots n$). Here and below relative units for all deviation 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 upper limit of variation for this parameter). Also we will use vector notation for sets of parameters (for example, (1, 0.5) is equivalent to $\delta p_1=1$, $\delta p_2=0.5$). Besides, all terms in the polynomial have to be invariant to the symmetry. For example if the positive and negative changes of parameter lead to the same spectrum changes only terms of odd power have to be considered.

If the modulus of maximal discrepancy between interpolated and MS calculated spectra exceeds 10% of the difference between ab-initio calculations for control point and spectrum calculated for initial set of the parameters ($\delta p_i=0$ ($i=1\dots n$)), then one has to include the corresponding term into the constructed interpolation polynomial. To calculate the energy dependent coefficient for this term a new equation corresponding to this control point is added into the system of equation solved by FitIt. Thus 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 to the required number of ab initio calculations since higher order cross terms are negligible if they are the product of any previously neglected term and another one.

In more details the logical sequence of steps of polynomial construction (see Fig. 2.) is the following:

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 3 nodes for single parameter interpolation (it can be controlled on step 4). Otherwise there is a risk to have 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 Angstrom 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: $\delta p_i = 1$, $\delta p_j = 0$, $j = 1\dots n$, $j \neq i$. 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 FeO_6 model molecule in Fig. 1). For such a parameter a linear term is equal to zero and thus one needs to use in the polynomial a second order.

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 following set of parameters:

$\delta p_i = 1, \delta p_k = 1, \delta p_j = 0, j = 1..n, j \neq i, j \neq k$. 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 influence of cross term on the result of interpolation, higher order terms with this couple of parameters and any other parameters can be negligible.

It can be that one parameter had symmetry (for example, parameter p_4 for 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 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 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 $\text{Ni}(\text{CN})_4$ model molecule).

Step 4 is the comparison of the results of interpolation as the function of each variable and multiple scattering calculations. Maximal deviation of interpolated spectrum from calculations using MS theory is expected for the following sets of the parameters: $\delta p_i = 0.5, \delta p_j = 0, j = 1..n, j \neq i$ (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 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 on step 3 and additional one-parameter terms included on step 4. The following control points have to be used: $\delta p_i = 1, \delta p_k = 0.5, \delta p_j = 0, j = 1..n, j \neq i, j \neq k$. In the case of linear first approximation corresponding terms are $\delta p_i \delta p_k^2$. For 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 single term: $\delta p_i \delta p_j^2 \delta p_k$. Due to this and to the fact that normally not all the cross terms between two variables are necessary, the number of subsequent terms (and therefore necessary multiple scattering calculations) decreases very rapidly. Analogous checks and improvements of polynomial have to be performed till the convergence is reached (there is no possibility to construct higher order terms within described above limitations). For real compounds it can be reached rather fast.

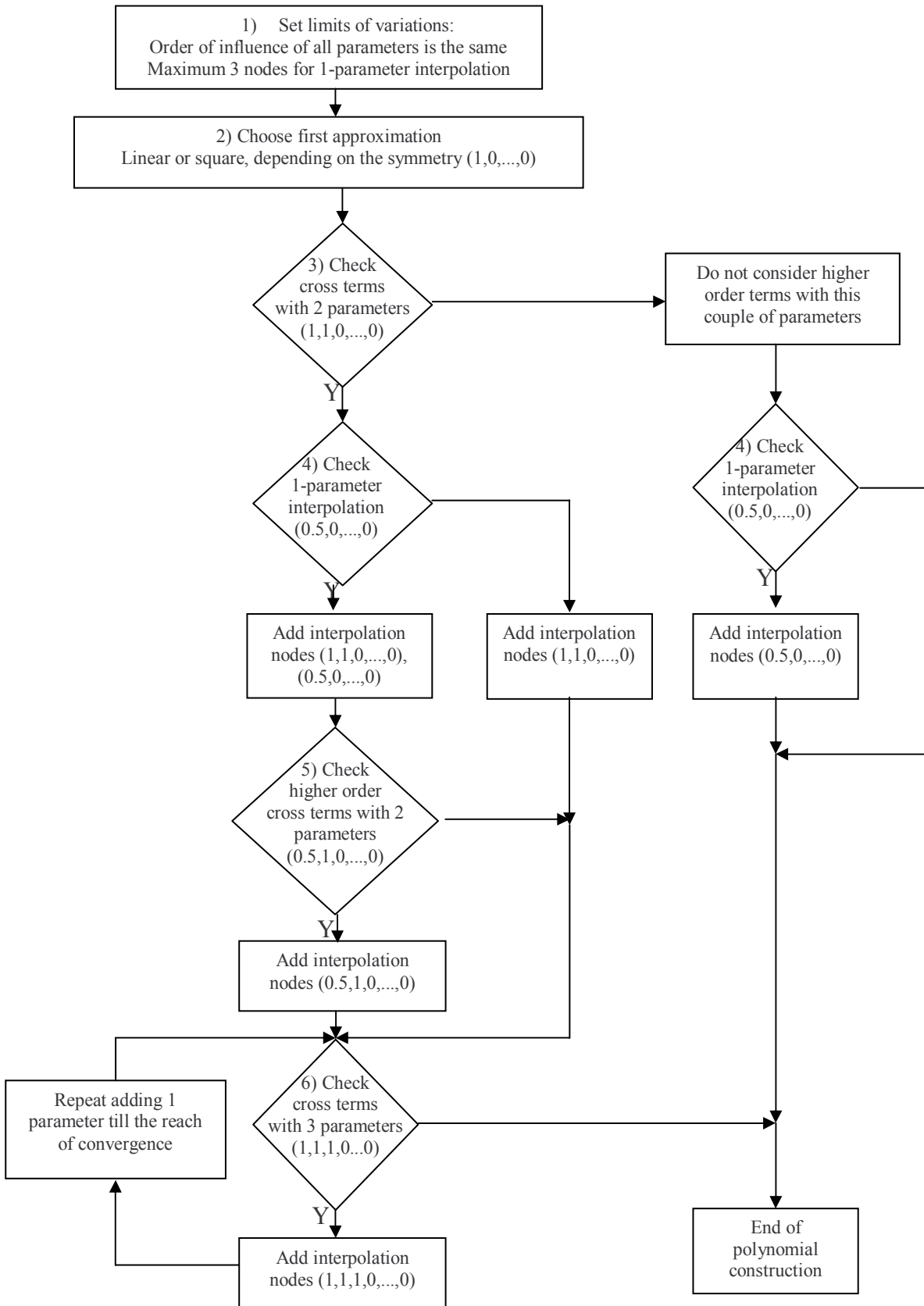


Fig. 2. Logical step-by-step sketch of polynomial construction strategy. Numbers of steps and examples of control points are shown in corresponding blocks.