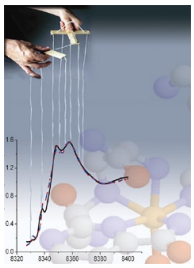

FitIt

Multidimensional interpolation approach

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To determine the structure of a compound under the study it is necessary to construct an initial structural model, which is rather close to the real structure, and to select the parameters of geometry, which will be varied. Then bond lengths and angles can be refined by varying them within rather small physical limits (for interatomic distances a typical value for such variation is about ±0.1 Å) minimizing the disagreement between theoretical and experimental XANES. For such refinement the following approach can be used.

In order to minimize the number of time-consuming ab-initio calculations of XANES an energy-dependent interpolation polynomial is constructed, which reproduces theoretical spectrum for all values of parameters within their possible limits. Ab-initio calculations of X-ray absorption spectra for different sets of parameters are performed at this stage only. External programs (FEFE 8.4, FDMNES etc.) can be used for such calculations as well as other external can be used to generate input file with transformed geometry.

After polynomial construction we search the minima of discrepancy between experimental spectrum and interpolated one varying structural parameters. Here we assume that the values of parameters, which correspond to the minimal discrepancy between experimental and theoretical spectra (which we will call the best fit parameters), are the closest to the values in real material under the study. Calculations of XANES using multidimensional interpolation are very fast and therefore optimization of strategy of multidimensional minima search is not very important. Thus simple gradient search of minima algorithm was used. To select global minimum from all local multidimensional minima this procedure repeats starting from different random points. As a result of the program execution one has the set of structural parameters and the spectrum, which correspond to the minimal discrepancy of theoretical and experimental XANES. All these steps are schematically shown in Fig.1.

To construct the interpolation polynomial we use the following expansion

$$\mu_i(E, p_1+\delta p_1, p_2+\delta p_2, ..., p_n+\delta p_n) = \mu(E, p_1, p_2, ..., p_n) + \sum_n A_n(E)\delta p_n + \\ + \sum_{m,n} B_{mn}(E)\delta p_m \delta p_n + ... \qquad (1)$$

Here $\mu_i(E)$ is the interpolated X-ray absorption coefficient, whereas $\mu(E)$ is the absorption coefficient calculated ab-initio. $\vec{p}^{\,0} = (p_1, p_2, ..., p_n)$ is a starting set of structural parameters and δp_n is a deviation of parameter p_n from the starting value. In many cases small number of terms is necessary since relatively small changes of structural parameters do not change the shape of XANES significantly. Therefore it is important to set physically reasonable limits of variations for all parameters, which are typically do not exceed ±0.1Å for bond lengths. Energy dependent coefficients $A_n(E), B_{mn}(E)...$ can be deduced from the results of ab-initio calculations of $\mu(E, \vec{p}^{\,k})$ for certain sets of structural parameters solving linear system of equations: $\mu_i(E, \vec{p}^{\,k}) = \mu(E, \vec{p}^{\,k})$. In this formula $\vec{p}^{\,k}$ is the set of structural parameters, which we will call

"interpolation node number k". Interpolated spectra $\mu_i(E, \vec{p}^k)$ contain coefficients, which have to be determined. The coefficients $A_n(E), B_{mn}(E)...$ do not depend on parameters deviations δp_n but they are different for alternative structural models (or values of parameters corresponds to the initial structure $\vec{p}^0 = (p_1, p_2, ..., p_n)$) To compare interpolated and experimental spectra two standard criterions were used: 1) mean square deviation $\frac{1}{E_2 - E_1}\int_{E_1}^{E_2}(\mu_i(E) - \mu_{\exp}(E))^2 dE$ or 2) Chebishev criterion $\max_{E_1<E<E_2}\left|\mu_i(E) - \mu_{\exp}(E)\right|$, where E_1 and E_2 are the energy limits of spectra comparison $\mu_i(E)$ is interpolated spectrum, $\mu_{exp}(E)$ is experimental one. The same normalization of all spectra (both experimental and theoretical) $\frac{1}{E_2 - E_1}\int_{E_1}^{E_2}\mu^2(E)dE = 1$ is used.

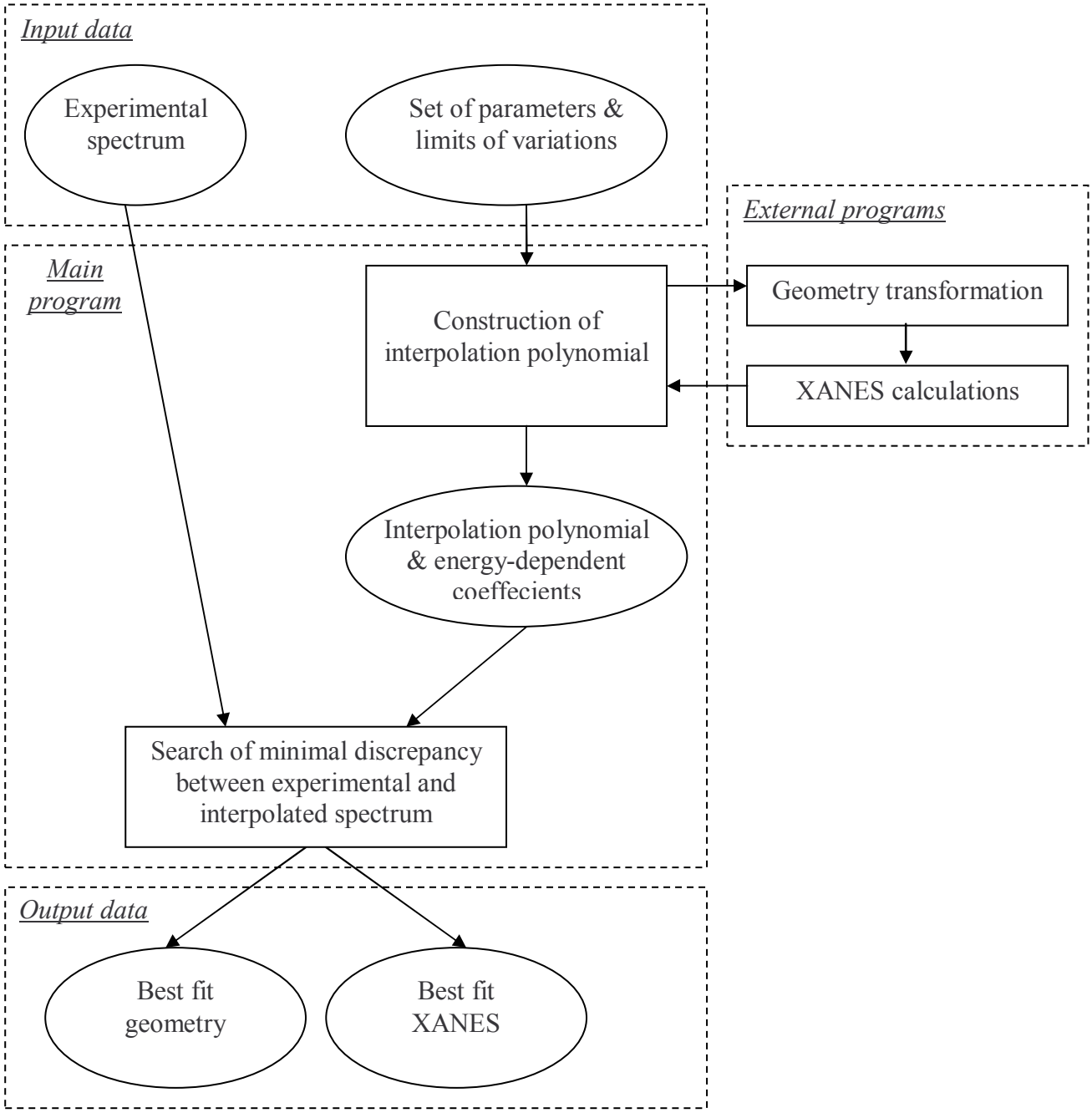

Fig. 1. Block diagram of the main parts of FitIt.