Practical approach to EXAFS Data Analysis

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Software for EXAFS analysis & simulations


Free Soft Index
- CDXAS
- CHOOS
- Daresbury
- EDA
- Fitt
- MAX
- EXAFSPAK
- GNXAS
- LASE
- MURATA
- NPI
- SEDEM
- TT-MULTIPLETS
- VIPER
- XAFS
- XAID
- XANES dactyloscope
  - IFEFFIT (Athena/Artemis/Feffit)
  - EXTRA
  - FDMNES

Commercial Soft Index
- Cenus2 XAFS
- Excurv98
- XDAP

Licensed Soft Index
- FEFF
- UWXAFS
- WINXAS
- XFIT

XAS Analysis Software Using IFEFFIT

The software on this page is freely available and free of cost. It runs on most platforms, including Linux, other UNIX, Windows, and MacOSX CDB. Easy-to-use shell scripts are available for many but not all common combinations of hardware and operating system.

Athena

Current release: 0.8.013
Release date: 15 December, 2008

Athena is an interactive graphical utility for processing EXAFS data. It handles most of the common data handling chores of interest, including deconvolution, aligning, merging, background removal, Fourier transforms, and more.

Artemis

Current release: 0.8.013
Release date: 15 December, 2008

Artemis is an interactive graphical utility for fitting EXAFS data using theoretical standards from mm and sophisticated data modeling along with linear least squares and statistical analysis. Artemis includes interfaces to Athena and Feffit.

XANES dactyloscope

Current release: 0.0.1
Release date: 5 September, 2006

Demeter

Demeter is a set of Perl programming tools for creating息息 applications.
EDAFORM: converts experimental data into the EDA's file format (ASCII, 2 columns).
EDAXANES: extracts the XANES part and calculates its first and second derivatives.
EDAEES: extracts the EXAFS part using improved algorithm for the atomic-like ("zero-line") background removal.
EDAFT: performs Fourier filtering procedure with or without amplitude/phase correction and with the rectangular, Gaussian, Kaiser-Bessel, Hamming and Norton-Beer F3 window functions.
EDAFIT: a non-linear least-squares fitting code, based on a high speed algorithm without matrix inversion. It uses the multi-shell Gaussian/cumulant model within single-scattering approximation and allows simultaneous analysis up to 20 shells with 8 fitting parameters ($N_i$, $S_o^2$, $R_i$, $\sigma_i^2$, $\Delta E_{0i}$, $C_{3i}$, $C_{4i}$, $C_{5i}$, $C_{6i}$) in each. The range of values for any fitting parameter can be limited by boundaries or fixed to a constant value. The covariance and correlation matrices can be also calculated.
EDARDF: a hybrid regularization/least-squares-fitting code allowing to determine model-independent radial-distribution-function (RDF) in the first coordination shell for a compound with arbitrary degree of disorder.
FTEST: performs analysis of variance of the fit results based on the Fisher's $F_{0.95}$-test.
EDAPLOT: general-purpose program for plotting, comparison and mathematical calculations frequently used in the EXAFS analysis (more than 20 functions !!!).
EDAFEFF: extracts the scattering amplitude and phase functions from FEFF****.dat files for use with EDAFIT or EDARDF codes (works under Windows).
A.Kuzmin, October 2011.

General scheme of the EDA package

- **EDAXANES**
  - XANES
    - \( \mu_x = \ln(I_0/I) \)
    - XAFS \( \chi(k) \)
    - FT \( \chi(k)k^n \)
      - BFT
        - j-shell XAFS \( \chi_j(k) \)
          - PARAMETRIZED MODEL
            - \( \chi(k, G(N_i, R_i, \sigma_i,...)) \)
          - GENERAL MODEL
            - \( \chi(k, G(R)) \)
    - \( \chi_{\text{fit}}(k) \)
      - RDF \( G(N_i, R_i, \sigma_i,...) \)
  - EXPEMENT
    - \( I_0, I \)

- **EDAFIT**
  - \( \chi_{\text{fit}}(k) \)
    - RDF \( G(R) \)
    - Reference (Experimental/Theoretical)
      - Am(k) & Ph(k)

- **FEFF+EDAFEFF**
  - FEFF
    - \( G(N_i, R_i, \sigma_i,...) \)
    - RDF

- **EDARDF**
  - REduced \( \chi'(k) \)
    - FT
      - RDF \( G(R) \)

- **EDAFT+EDAPLOT**
  - EDAPLOT
  - FTEST

- **EDAFORM**
  - EDAEES
**EDAEES: Extraction of EXAFS Signal**

**STEP 1:**

\[ \chi(E) = \frac{\mu_{\text{exp}}(E) - \mu_b(E) - \mu_0(E)}{\mu_0^l(E)} \]

**STEP 2:**

\[ \mu_b(E) = A - \frac{B}{E^3} \]

\[ \mu_0(E) = \mu_0^l(E) + \mu_0^{\text{II}}(k) + \mu_0^{\text{III}}(k) \]

\[ k = \sqrt{(2m_e/h^2)(E - E_0)} \]

\[ \begin{align*}
\mu_0^l(E) &= P_n(E) \\
\mu_0^{\text{II}}(k) &= P_m(k) \\
\mu_0^{\text{III}}(k) &= S_3(k, p)
\end{align*} \]

\[ n = 2, \ldots, 4 \]

P\text{ }_n – polynomial of n-order

S\text{ }_3 – smoothing cubic spline

A.Kuzmin, October 2011.
**STEP 3:**

\[ \mu^I(k) = \mu(E) - \mu_0^I(E) \]

\[ \mu_0^{II}(k) = P_m(k) \]

\[ m = 1, \ldots, 7 \]

**STEP 4:**

\[ \mu^{II}(k) = \mu^I(k) - \mu_0^{II}(k) \]

\[ \mu_0^{III}(k) = S_3(k, p) \]

\[ p \geq 0 - \text{smoothing spline parameter} \]
**EDAEEES: Extraction of EXAFS Signal**

**STEP 5:**

\[
\mu_0(E) = \mu_0^I(E) + \mu_0^{II}(k) + \mu_0^{III}(k)
\]

Influence of zero-line on the EXAFS.

\[
\chi(E) = \frac{\mu_{\exp}(E) - \mu_b(E) - \mu_0(E)}{\mu_0^I(E)}
\]
EDAEES: Extraction of EXAFS Signal

Influence of zero-line removal on the FT of the EXAFS.

A.Kuzmin, October 2011.
Fourier transform (FT)

\[ FT(R) = \sqrt{\frac{2}{\pi}} \int_{k_{\text{min}}}^{k_{\text{max}}} \chi(k) k^n W(k) \exp(-2i k R) dk \]

Window function \( W(k) \):

\[ W(k) = 1 \]  
(Rectangular),

\[ W(k) = J_0(\pi A \sqrt{1 - (1 - k/\bar{k})^2})/J_0(\pi A) \]  
(Kaiser – Bessel),

\[ W(k) = \exp(-0.5 \pi A (1 - k/\bar{k})^2) \]  
(Gaussian),

\[ W(k) = \begin{cases} 
0.025 + 0.5[1 - 0.95 \cos(\pi (k - k_{\text{min}})/A)] & \text{for } k < k_{\text{min}} + A \\
0.025 + 0.5[1 + 0.95 \cos(\pi (k - k_{\text{max}} + A)/A)] & \text{for } k > k_{\text{max}} - A \\
1.0 & \text{otherwise}
\end{cases} \]  
(Hamming),

\[ W(k) = 0.045335 + 0.554883[1 - (1 - k/\bar{k})^2]^2 + 0.399782[1 - (1 - k/\bar{k})^2]^4 \]  
(Norton – Beer F3),

\[ W(k) = \exp(-(k - \bar{k})^2/(\bar{k} \ln(0.1))) \]  
(Gaussian 10%),
Back-Fourier transform (BFT)

\[ BFT(k) = \frac{1}{W(k)} \sqrt{\frac{2}{\pi}} \int_{R_{\text{min}}}^{R_{\text{max}}} FT(R) \exp(2ikR) dR \]

\[ AMPL(\chi(k)) = \sqrt{\Im(BFT(k))^2 + \Re(BFT(k))^2} \]

\[ PHASE(\chi(k)) = \arctan(\Im(BFT(k))/\Re(BFT(k))) \]
Influence of backscattering amplitude and phase on EXAFS and FT

N.B. The RDF G(R) is the same for each atoms pair!

FEFF8 simulations for the Ni K-edge
Simulation of the EXAFS signal

The EXAFS signal $\chi(k)$ can be described by the following equations depending on the way how the RDF $G(R)$ is described.

1. The parametrized multi-component Gaussian/cumulant model (EDAFIT):

$$
\chi_{\text{model}}(k) = S_0^2 \sum_{s} \frac{N_i}{kR_i^2} f_i(\pi, k, R_i) \exp\left(-2\sigma_i^2 k^2 + \frac{2}{3} C_4 i k^4 - \frac{4}{45} C_6 i k^6\right) \\
\times \exp(-2R_i/\lambda(k)) \sin(2kR_i - \frac{4}{3} C_3 i k^3 + \frac{4}{15} C_5 i k^5 + \phi_i(\pi, k, R_i))
$$

2. The general RDF model (EDARDF):

$$
\chi_{\text{model}}(k) = S_0^2 \int_{R_{\text{min}}}^{R_{\text{max}}} \frac{G(R)}{kR^2} f(\pi, k, R) \sin(2kR + \phi(\pi, k, R)) dR
$$

3. The splice model (EDAPLOT + EDAFT):

$$
G(R) = -(R^2/S_0^2) \text{Im} \int_0^{k_{\text{max}}} k\chi_1(k) \frac{\exp(-i\Phi(\pi, k, R))}{F(\pi, k, R)} \exp(-2ikR)dk \\
= \int_0^{k_{\text{min}}} (...)dk + \int_{k_{\text{min}}}^{k_{\text{max}}} (...)dk + \int_{k_{\text{max}}}^{+\infty} (...)dk.
$$

Reconstructed from cumulant Experimental $=0$
Where to get amplitude $f(\pi, k, R)$ and phase $\phi(\pi, k, R)$?

- Ab initio theory: FEFF8, ...

- Reference compound: a crystal with well known structure

\[ f(k) = A M P L(\chi_{\text{ref}}(k)) \frac{kR^2}{N} \]
\[ \phi(k) = P H A S E(\chi_{\text{ref}}(k)) - 2kR \]
Gaussian/cumulant parametrization of the EXAFS signal

\[
\chi(k) = S_0^2 \sum_{i=1}^{M} \frac{N_i}{k R_i^2} f_i(\pi, k, R_i) \exp(-2\sigma_i^2 k^2 + \frac{2}{3} C_4 i^4 - \frac{4}{45} C_6 i^6) \exp\left(-\frac{2R_i}{\lambda(k)}\right) \times \sin\left(2kR_i - \frac{4}{3} C_3 i^3 + \frac{4}{15} C_5 i^5 + \phi_i(\pi, k, R_i) + 2\delta_c(k) - l\pi\right)
\]

\[k = \sqrt{(2m_e / \hbar^2)\Delta E_0}\]

Correlation between parameters

in the amplitude of EXAFS function: \(S_0^2N, \sigma^2, C_4, C_6\)
in the phase of EXAFS function: \(R, C_3, C_5, \Delta E_0\)

Example:

\[\Delta E_0 = 1 \text{ eV} \Rightarrow \Delta R \approx 0.005 \text{ Å} \quad \Delta N = 0.5 \Rightarrow \Delta \sigma^2 \approx 0.001 \text{ Å}^2\]
\[\Delta E_0 = 5 \text{ eV} \Rightarrow \Delta R \approx 0.025 \text{ Å} \quad \Delta N = 1.0 \Rightarrow \Delta \sigma^2 \approx 0.002 \text{ Å}^2\]
\[\Delta E_0 = 10 \text{ eV} \Rightarrow \Delta R \approx 0.048 \text{ Å}\]

1. Fix \(E_0\)
2. Fix \(N\)
Relationship between the $k$ and $R$ space 
Nyquist theorem

From the properties of Fourier transform:

if $\chi(k)$ is given in the $k$-space from $k_{\text{min}}=0$ to $k_{\text{max}}$ with a step $dk$, then $G(R)$ will be given in the $R$-space from $R_{\text{min}}=0$ to $R_{\text{max}}=\pi/2dk$ with the spatial resolution $\delta R \approx 1/2k_{\text{max}}$.

For example: $\delta R = 0.03$ Å for $k_{\text{max}} = 16$ Å$^{-1}$.

The total number of parameters $M_{\text{max}}$ used in the model must be less than that given by the Nyquist theorem:

$$M_{\text{max}} = \frac{2\Delta k \Delta R}{\pi} + 2$$

For a single shell, $\Delta k = k_{\text{max}} - k_{\text{min}} = 15$ Å$^{-1}$ and $\Delta R = R_{\text{max}} - R_{\text{min}} = 1$ Å, then $M_{\text{max}} \approx 11.5$.

**Fisher’s $F_{0.95}$ test**

The FTEST program allows one to perform the analysis of variance of the results of the multi-shell fit using the Fisher’s $F_{0.95}$ test.

- The experimental EXAFS $\chi_{\text{exp}}(k)$ is given from $k_{\text{min}}$ to $k_{\text{max}}$ and corresponds to the range of the back-Fourier transform $\Delta R$.
- It was fitted by two models $\chi_1(k)$ and $\chi_2(k)$ having the number of fitting parameters $M_1$ and $M_2$.

The variance is

$$D = \frac{M_{\text{max}}}{N(M_{\text{max}} - M_{\text{fit}})} \sum_{i=1}^{N} \left( \chi_{\text{exp}}(k_i) - \chi_{\text{model}}(k_i) \right)^2$$

According to the Fisher’s $F_{0.95}$ test (95% probability), the second model should be accepted when

$$\frac{D_{\text{fit1}}}{D_{\text{fit2}}} > F_{0.95}$$

Example of Fisher’s $F_{0.95}$ test

Analysis of the experimental Re L$_3$-edge EXAFS $\chi_{\text{exp}}(k)$ from the first coordination shell (Re-O$_1$) in ReO$_3$.

Back-FT in the interval from $R_{\text{min}}=0.7$ Å to $R_{\text{max}}=2.1$ Å: $\Delta R=1.4$ Å.

Best-fit of $\chi (k)$ in the interval from $k_{\text{min}} = 1.5$ Å$^{-1}$ to $k_{\text{max}} = 15$ Å$^{-1}$.

Model1 $\chi_1(k,N,R,\sigma^2,\Delta E_0)$: the number of fitting parameters $M_1=4$.
Model2 $\chi_2(k,N,R,\sigma^2,\Delta E_0,C_3,C_4,C_5,C_6)$: the number of fitting parameters $M_2=8$.

The variance is

$$D = \frac{M_{\text{max}}}{N(M_{\text{max}} - M_{\text{fit}})} \sum_{i=1}^{N} \left( \chi_{\text{exp}}(k_i) - \chi_{\text{model}}(k_i) \right)^2$$

$$\frac{D_{\text{fit1}}}{D_{\text{fit2}}} > F_{0.95}$$

$D_1=4.02 \times 10^{-4}$ and $D_2=6.37 \times 10^{-4}$, so $D_1/D_2=0.63 < F_{0.95} = 4.1$

According to the Fisher’s $F_{0.95}$ test, the second model should not be accepted!
Amplitude ratio and phase difference analysis within the Gaussian/cumulant approximation

This method can be used to find relative variations of parameters in the EXAFS formula when the single shell EXAFS signal can be isolated.

\[
\ln \frac{AMPL(k)}{AMPL_{et}(k)} = \ln \frac{NR^2_{et}}{N_{et}R^2} - 2k^2(\sigma^2 - \sigma^2_{et}) + \frac{2}{3}k^4 \Delta C_4
\]

\[
PHASE(k) - PHASE_{et}(k) = 2k(R - R_{et}) - \frac{4}{3}k^3 \Delta C_3.
\]

EXAFS Data Analysis: how to do?

Crystal structure model

ATOM

FEFF8

EDAFEFF

amp***.dat
pha***.dat

EDAEES

χ(k)

Compare

χ(k)

Change E₀

Change E₀

χFEFF(k)

Wavenumber k (Å⁻¹)

Distance R (Å)

EXAFS

χ(k)k² (Å⁻²)

Wavenumber k (Å⁻¹)

ATOMIC

χ(k)

Change E₀

Phase

χ(k)
Examples of EXAFS data analysis by different approaches
Gaussian, cumulant and RDF models

(a) RDF model

(b) Gaussian-model
Cumulant-model
RDF model

(c) “experiment”
model RDF

(d) Gaussian-model
Cumulant-model
RDF model

The RDFs derived by the splice and RDF techniques for several $k_{\text{max}}$ values

Dashed line – splice method
Solid line – RDF method
Circles – “experiment” (model RDF)

The RDFs for the 1st shell in ReO$_3$, WO$_3$ and MoO$_3$ derived by the splice and RDF techniques

Dashed line – experiment
Solid line – RDF method
Dotted line – splice method
Examples of best fits of the EXAFS signals in $k$-space

**EDAFIT (Gaussian model)**

| $k$ (Å$^{-1}$) | $\chi(\mathbf{k}|\mathbf{k}^2$ | $T,K$ |
|---------------|----------------|-------|
| 383           | 613            | 513   |
|               | 668            |       |

**EDARDF**

| $k$ (Å$^{-1}$) | $\chi(\mathbf{k}|\mathbf{k}^2$ | $T,K$ |
|---------------|----------------|-------|
| 383           | 613            | 513   |
|               | 668            |       |

Re $L_3$-edge in rhenium trioxide ReO$_3$

Examples of best fits of the EXAFS signals in \( k \)-space by EDAFIT (Gaussian model)

Ni \( K \)-edge in polycrystalline and thin film nickel oxide NiO

Solid lines – experiment, dashed lines - model

Examples of best fits of the EXAFS signals in $k$-space

EDAFIT (Gaussian model)

EDARDF

Ag $K$-edge in Ag$_2$O-B$_2$O$_3$ glasses

Dashed lines – experiment, solid lines - model

Thank you for attention!

Get more details at:

http://www.dragon.lv/eda
and

http://www.dragon.lv/exafs