FITEXA2009
short manual

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Fitexa2009 code exploits the MINUIT subroutines to refine EXAFS data via a least-square procedure. The program requires input parameters and refinement commands in the file *fitexa.inp* which is composed of tre main sections:

A: Definition of parameters

B: Input experimental data and definition of theoretical contributions

C: Refinement commands (MINUIT commands)

A: definitions of refinement parameters

This section contains the standard parameter definition cards as required by MINUIT subroutines (see MINUIT manual for further reading). An example of parameter definition cards is the following:

```
***param-N|*param***|****value|****error|******min|******max      CARD \# A.0
         1    n1         1.000      .000      0.00      5.00      CARDs \# A.1
         2    r1         2.050      .001      1.90      2.10
         3    s1         0.003     .0001      0.00      0.10
         4    de         0.000      .100    -10.00     10.00
         5    gamma      0.000      .000      0.00      5.00
         6    so2         1.00      .000      0.00      5.75
                                                                 CARD \# A.2
```

\# **A.0** [C60] is the title card.

\# **A.1** [I10,C10,4F10] are the cards defining each parameter to be used in the refinement. Each card contains 6 fields:

- \# **A.1.i** (Integer) the parameter number, this number will be used to call this parameter in the program;
- \# **A.1.n** (10 characters) the parameter name;
- \# **A.1.V** (Float) the initial parameter value used in the refinement;
- \# **A.1.D** (Float) the estimated error on the parameter, if zero the parameter will be kept fixed, otherwise it will ve varied with steps related it (see MINUIT manual for more details)
- \# **A.1.min** (Float)lower limit for the parameter value variation (optional);
- \# **A.1.max** (Float) upper limit for the parameter value variation (optional) (see the MINUIT manual for details on how MINUIT treat the parameter limits);

\# **A.2** An empty line is mandatory to signal the end of A cards.

WARNING: the **A** cards are formatted, then do not use *tab* in between the fields, use *spaces* instead.

B: Main input

'EXAFS_file_name'	CARD # B.1	EXAFS file name	(C80)
ABCD	CARD # B.2	Output file leading extension	(C4)
C_k,$C_{k\chi}$	CARD # B.3	Columns for k, and $k\chi(k)$	(2I)
k_{min},k_{max}	CARD # B.4	K-limits for data refinement	(2F)
wgt	CARD # B.5	Exponent for k weighting: k^{wgt}	(2F)
NSo	CARD # B.6	Parameter number for S_o^2	(I)
NS	CARD # B.7	number of shells to be used	(I)
FT_flg	CARD # B.8	Amp. and ph. filtering flag	(Y/N)
K_m K_M F_{wg} F_t F_w R_m δ_R R_L R_R	CARD # B.9	info for Fourier transform and filter	
	Follow NS cards, one for each contribution		
S_t	CARD # B.10.1	shell type (G,M,C)	(ch1)
N_{Cn_s},M_{Cn_s}	CARD # B.10.2	Coordination number	(I,F)
N_{R_s}	CARD # B.10.3	Shell distance Par. Num.	(I)
$N_{\sigma_s^2}$	CARD # B.10.4	Debye Waller Par. Num.	(I)
$N_{\Delta E_o}$,N_γ	CARD # B.10.5	Energy shift and γ Par. Num.	(2I)
AF_t	CARD # B.10.6	Amplitude and phase file type	(C)
'AF_file'	CARD # B.10.7	Amplitude and phase file	(C)
σ_χ	CARD # B.11	Statistical Error on $\chi(k)$	(F)

The best fit is obtained minimizing the function:

$$F \propto \sum_i W_i \left(k^{wgt} (\chi_i^{th} - \chi_i^{exp}) \right)^2$$

W_i being constants, variable W_i is under test.

 # B.1 [C80] Name of the data file. Is must be multi-column ASCII file containing at least the k and the $k\chi(k)$ data column. If maybe a raw EXAFS data (*name*.exa from ESTRA2009 or any other EXAFS data extraction) or Fourier filtered data (*name*.bf from ESTRA2009 or any other EXAFS data extraction). Header lines are skipped if starting with "# ". Errors may arise if comments or empty lines are find during the data reading.

 # B.2 [4C] 4-character leading extension for output files which will be named **ABCD**.*ext* (see below for details).

 # B.3 [2I] Column numbers for k and $k\chi(k)$ in the data file.

 # B.4 [2F] K-range for data fitting.

 # B.5 [F] K-weight (wgt) for data fitting.

 # B.6 [I] Parameter number to be used for S_o^2 parameter in the standard EXAFS formula.

B.7 [I] Number of shells to be used.

B.8 [C1] Fourier filtering flag (Y or N): fitting Fourier filtered data using theoretical Amplitude and Phase data requires to apply the same Fourier filter window also the theoretical Amplitude and Phase data, so use Y in that case, otherwise N should be used. In order to properly filter the theoretical amplitude and phase functions use the same parameters (K range, R range, apodization window) used for data filtering. The remaining part of the string, after the first character, only contains info about the fields to be input on the next card. Remember that the fitting is performed on the k-space, the real space plots give intuitive picture of the fitting but they are only FT of experimental data and theoretical functions.

B.9 [3F,I,5F] parameters for Fourier transform to be applied to experimental and theoretical $\chi(k)$. If # B.8=Y parameters for Fourier filtering to be applied to Amplitude and phase functions.
K_m K_M: limits for FT, il 0,0 the fitting limits will be applied;
F_{wg}: $k^{F_{wg}}$ weight to be applied to the FT transform of experimental and fitted EXAFS;
F_t F_w: Type of apodization window to be applied (F_t=0 none, F_t=1 Hanning, F_t=2 Gauss) and apodization width;
R_m δ_R: maximum R value and R mesh for Real space calculation;
R_L R_R: limits for the Fourier filtering.

B.10 NS cards defining the contributions to the theoretical EXAFS function:

B.10.1 [C1] model for the neighbour shell: G= Gaussian, M= Metallic glasses (ref..), C= Cumulant expansion (it will require an additional # B.10.5b card after the B.10.5 card. The Gaussian distribution calculate the theoretical EXAFS signal of the s-th shell as:

$$k\chi_s = \frac{S_o^2 \, N_s}{R_s^2} \, A(k) \sin\left(2kR_s + \phi(k)\right) \, \exp(-2R_s/\lambda) \, \exp(-2k^2\sigma_s^2)$$

Using the cumulant expansion the theoretical EXAFS signal of the s-th shell is calculated as:

$$k\chi_s = \frac{S_o^2 \, N_s}{R_s^2} \, A(k) \sin\left(2kC_1 - \frac{4}{3}k^3 C_3 + \phi(k)\right) \, \exp(-2R_s/\lambda) \, \exp(-2k^2\sigma_s^2 + 2k^4 C_4/3)$$

with $C_1(k) = R_s - 2\frac{\sigma_s^2}{R_s}\left(1 + \frac{R_s}{\lambda(k)}\right)$ The parameter R_s reported in the output file is the interatomic distance of the *effective* distribution, accordingly to P. Fornasini et al. J. Phys. Cond. Mat. **13**, 7859 (2001). The Real $R_s^r = R_s + 2\sigma^2/R_s(1 + R_s/\lambda)$ (the average λ must be calculated... to be done! the error is around 2×10^{-3})

B.10.2 [I,F] parameter number for coordination number N_{C_n} (Integer) and multiplicity M_{Cn_s}. N_s is calculated as the value of the parameter number N_{C_n} by M_{C_n}. Instead of using N_{Cn_s} and M_{Cn_s}, N_s can be evaluated using a more flexible expression involving constants and MINUIT parameters to be evaluated at each refinement step. The expression string must be enclosed in between & symbols, the parameter i-th is addressed by # i. For example the expression:
& 6 - #3 * 6 &
evaluates the $N_s = 6(1 - x)$, where x is the value of the parameter 3 (see A CARDS). Only basic operators are allowed: +, -, *, /, and ^ without parentheses.

B.10.3 [I] parameter number for shell distance N_{R_s}. As for N_s the distance can be evaluated using a simple mathematical expression enclosed in between & symbols. For example the

expression:
& #10 * 2ˆ0.5 &
evaluates the $R_s = a\sqrt{2}$, where a is the value of the parameter 10 (see A CARDS).

B.10.4 [I] parameter number for Debye-Waller factor σ_s^2. As described above the σ_s^2 can be calculated using a mathematical expression enclosed in between & symbols.

B.10.5 [2I] parameter number for Energy shift and γ. Gamma is used to evaluate the empirical mean free path parameter λ of the standard EXAFS formula. Is *feff* amplitude and phase functions are used, it must be zero.

B.10.5b [2I] This card appears only if **B.10.1 = C** and are the parameter numbers (A CARDS) of second and third cumulants to be used for the Cumulant EXAFS model. No mathematical expressions are allowed for them.

B.10.6 [4C] amplitude and phase file type: i) *feff*: are the feff****.dat files. ii) *exp1*: experimental amplitude A_{exp} ϕ_{exp} and phase functions obtained, for example, from ESTRA2009 code. iii) *exp2*: as emphexp1 a column for mean-free path is required. This is used for Cumulant expansion EXAFS formula.

B.10.6b [3-4I] if *exp1* columns for k, A_{exp}, ϕ_{exp}; if *exp2* columns for k, A_{exp}, ϕ_{exp} and mean free path L.

B.10.7 [C80] Amplitude and phase file name.

B.11 [f] statistical analysis option:

0<B.11<1 This constant value is the statistical error on $\chi(k)$ is: $\sigma_\chi = C$. This value can be evaluated from the ESTRA2009 output files. The refinement weights $W_i = 1$ are used.

|B.11| >1 The σ_i on each point are evaluated as $\sigma_i = \chi - \chi'$, χ' being a smooth function trough the data calculated Fourier filtering the experimental χ in the R-space in between 0 and $R_{max} = |\text{B.11}|$. If B.11 > 1 the constant $\sigma_\chi = \sqrt{(\sum_i \sigma_i)/N}$ is used and the refinement weights $W_i = 1$ are used. If B.11 < -1 each point in the fitting is weighted by $W_i = \sigma_\chi/\sigma_i$ but this option is under test.

B.11=0 The smooth function χ' is evaluated using high degree splines trough the data, and the average σ_χ is calculated as above and applies to all data.

B.11=-1 As above but the fitting is weighted by $W_i = \sigma_\chi/\sigma_i$. This option is under test.

C: MINUIT commands

Refer to the MINUIT manual for them [**http://www.phy.hr/˜npaar/Math_Mod/minuit.pdf** or **http://wwwasdoc.web.cern.ch/wwwasdoc/minuit/minmain.html**]

Output files

fit.plt Contains the macro to be loaded by Gnuplot for rapid look at the fitting results. Use the command **load 'fit.plt'** on Gnuplot. You can modify and rename it to have different graphics or postscript output (see Gnuplot manual for advanced Gnuplot use).

***ABCD*.out** output parameters and statistical information.

***ABCD*.fit** Multicolumn ASCII file with experimental and best fit. Columns contains: 1:$K(\text{Å}^{-1})$ 2:$k\chi_{exp}$ 3:$k\chi_{th}$ 4:$k(\chi_{exp} - \chi_{th})$ 5:$k^{wgt}\chi_{exp}$ 6:$k^{wgt}\chi_{th}$ 7:$k^{wgt}(\chi_{exp} - \chi_{th})$ 7:$w_i =< \sigma^2 > /\sigma_i$

***ABCD*.fou** Multicolumn ASCII file with Fourier transform of experimental and best fit. The columns contain: 1:R 2:$|FT| of \chi_{exp}$ 3:$Imm(FT) of \chi_{exp}$ 4:$|FT| of \chi_{th}$ 5:$Imm(FT) of \chi_{th}$

***ABCD*.par** Partial χ_s contributions used in the fit.

***ABCD*_Abs.fou** Moduli of FT of the partial contributions used in the fit.

***ABCD*_Imm.par** Imaginary parts of the FT of the partial contributions used in the fit.

***ABCD*.his** Values of the parameters during the refinement. 1:refinement steps, 2:F, 3:.... parameters

fitexa.log Log file. Look at this file for MINUIT refinement info, Contour plots, error bars and so on.

fitexa.sav MINUIT parames and covariance matric after SAVE command.

Statistical Infos on *ABCD*.out file

Wgt_signal : k^w-weighted average signal amplitude:

$$S_w = \sqrt{\frac{1}{N}\sum_i [k^w \chi_i]^2}$$

signal : average $\chi(k)$ amplitude:

$$S_o = \sqrt{\frac{1}{N}\sum_i [\chi_i]^2}$$

variance : average $\chi(k)$ variance $< \sigma^2 >$.

std.dev : average $\chi(k)$ standard deviation $< \sigma >= \sqrt{< \sigma^2 >}$.

wgt.var. : average $k^w\chi(k)$ variance:

$$< \sigma_w^2 >= \frac{1}{N}\sum_i [k^w \sigma_i]^2$$

wgt.std.dev : average $k^w\chi(k)$ standard deviation:

$$< \sigma_w >= \sqrt{\frac{1}{N}\sum_i [k^w \sigma_i]^2} = \sqrt{< \sigma_w^2 >}$$

<**S/N**> : Unweighted signal to noise ratio:

$$< S/N >= \sqrt{\frac{1}{N < \sigma^2 >}\sum_i [\chi_i]^2} = \frac{S_o}{< \sigma >}$$

<**WS/N**> : k^w weighted signal to noise ratio:

$$< WS/N >= \sqrt{\frac{1}{N < \sigma_w^2 >} \sum_i [k^w \chi_i]^2} = \frac{S_w}{< \sigma_w >}$$

F : minimized function

$$F \propto \sum_i W_i \left(k^w (\chi_i^{th} - \chi_i^{exp})\right)^2$$

W_i being constants or variable $(1/error_i)$

R^2 : Normalized residual:

$$R^2 = \frac{\sum_i [k^w (\chi_i - \chi_i^{th})]^2}{\sum_i [k^w \chi_i]^2}$$

R0^2 : Normalized residual, unweighted:

$$R_o^2 = \frac{\sum_i [(\chi_i - \chi_i^{th})]^2}{\sum_i [\chi_i]^2}$$

reduced_ Chi^2 reduced χ_ν^2 for k^w-weighted data:

$$\chi_w^2 = \frac{1}{N-p} \frac{\sum_i k_i^{2w} \left[\chi(k_i) - \chi_{th}(k_i)\right]^2}{< \sigma_w^2 >}$$

reduced_ Chi^2$_0$ reduced χ_ν^2 for unweighted data:

$$\chi_o^2 = \frac{1}{N-p} \frac{\sum_i \left[\chi(k_i) - \chi_{th}(k_i)\right]^2}{< \sigma^2 >}$$

Suggested errdef : value to be used in MINUIT for a given confidence interval using the command:

```
set errdef #####
```