New features in

WinXAS version 3.2

(Released Feb. 09)

Significance of structural parameters in XAFS data analysis

In conventional XAFS data analysis scattering amplitudes and phases are either calculated for a suitable model structure or obtained from references. Subsequently, a sum of theoretical XAFS functions is refined to the experimental data. Structural parameters like coordination numbers (CN), nearest neighbor distances (R), and disorder parameters (e.g. σ^2) may be determined. However, more often than not, the number of potential parameters exceeds the number of "independent" parameters. The upper limit may be calculated from Fourier theory and must not be exceeded. Nonetheless, it appears that even refinements employing a much smaller number of freely varied parameters may yield ambiguous structural results. Basically, one pair of strongly correlated parameters suffices to render a seemingly good agreement between experimental data and theoretical model structure meaningless. Hence, procedures are sought that enable evaluating the significance of each fitting parameter individually.

Three steps to evaluating XAFS refinements

1) The number of independent parameters (N_{ind}) may be calculated according to the Nyquist theorem (e.g. $N_{ind} = 2/\pi * \Delta R * \Delta k$). Normally, the number of free running parameters in the refinements should be well below N_{ind}.

N_{ind} is given in the *Enter XAS Parameters* box (4.5.16) and listed in the *Result window*.

(Confidence limits and F tests may be calculated automatically after a XAFS refinement or chosen from the *Numeric* menu. Note that calculations may take several minutes!)

2) Confidence limits can be calculated for each individual parameter. In the corresponding procedure, one parameter is successively varied by a certain percentage (i.e. 0.05 % for R and 5 % for σ^2) and the refinement is restarted with this parameter kept invariant. The parameter is repeatedly increased or decreased until the fit residual exceeds the original fit residual by more than 5 %. Eventually, the confidence limit of the parameter is obtained from linear

interpolation between the last and second last increment for an increase in fit residual of 5 %. This procedure is consecutively performed for each fitting parameter.

3) A so-called F test is performed to assess the significance of the effect of additional fitting parameters on the fit residual. The corresponding procedure was adopted from the well-known library "*Numerical Recipes in C*" where it is described in detail. In short, one parameter is again varied by a certain percentage (i.e. between 2 and 8 % for R and between 10 and 80 % for σ^2) and the refinement is restarted with this varied parameter kept invariant. Subsequently, the difference between experimental and theoretical function (i.e. magnitude and imaginary part of FT(χ(k)*k^3) for a refinement in R space) is calculated and compared to that of the original refinement (*F test*). The corresponding F parameter ranges between 0.0 and 1.0, where F = 1.0 indicates an insignificant change in the fit residual, while F = 0.0 indicates a highly significant change in fit residual. The iterative procedure is terminated when the corresponding F parameter was below 0.7. Fit parameters with F = 0.8 or higher are most likely strongly correlated and may be statistically insignificant. These parameters should be kept invariant in the refinement. Eventually, this procedure was also consecutively performed for each fitting parameter.

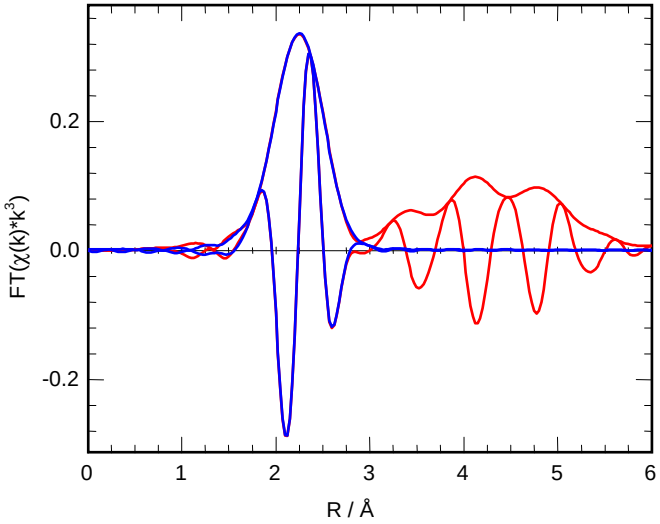
Rough estimate:	0	<	F	<	0.2	independent
	0.2	<	F	<	0.5	largely independent
	0.5	<	F	<	0.8	maybe dependent
	0.8	<	F	<	1.0	dependent

Examples:

i) Cu metal foil, Cu K edge XAFS spectrum,

theoretical phase and amplitude calculated for first Cu – Cu shell with FEFF 7.

(R range 1.7 - 2.9 Å, k range 2.1 - 12.8 $Å^{-1}$, residual 1.05, N_{ind} = 10, N_{free} = 4)



Showcase example: very good fit, clearly independent parameters (all F=0) and very small confidence limits for all parameters refined.

```
-- Automated F-test for current fitting parameters -  Original R value:  1.047
Par #02:   11.66        - F 0    , R:  1.882 (R: 1.047, Par: 12.826   , Var: 10  %)  : independent
Par #03:   2.5437       - F 0    , R:  21.52 (R: 1.047, Par: 2.5946   , Var: 2   %)  : independent
Par #04:   0.0081079    - F 0    , R:  3.535 (R: 1.047, Par: 0.0097295, Var: 20  %)  : independent
Par #05:   3.9593       - F 0    , R:  2.148 (R: 1.047, Par: 4.7512   , Var: 20  %)  : independent
```

(1) (2) (3) (4) (5) (6) (7) (8)

(1) # of free running parameter in refinement corresponds to parameter list

(2) fit parameter obtained from original refinement

(3) F test parameter and (8) the corresponding significance estimate

(4) residual obtained from fit with value of varied parameter ((6) varied by X % (7) with respect to original fit) kept invariant in the refinement

(5) residual obtained from allowing the modified parameter (6) to vary in fit (should be the same as original residual, otherwise local minimum).

```
-- Confidence limits of current fitting parameters -
Variation of residual within 95 %
Par #02:   11.66015       +-  0.157
Par #03:   2.543684       +-  0.000554
Par #04:   0.008107939    +-  0.000105
Par #05:   3.959325       +-  0.108
```

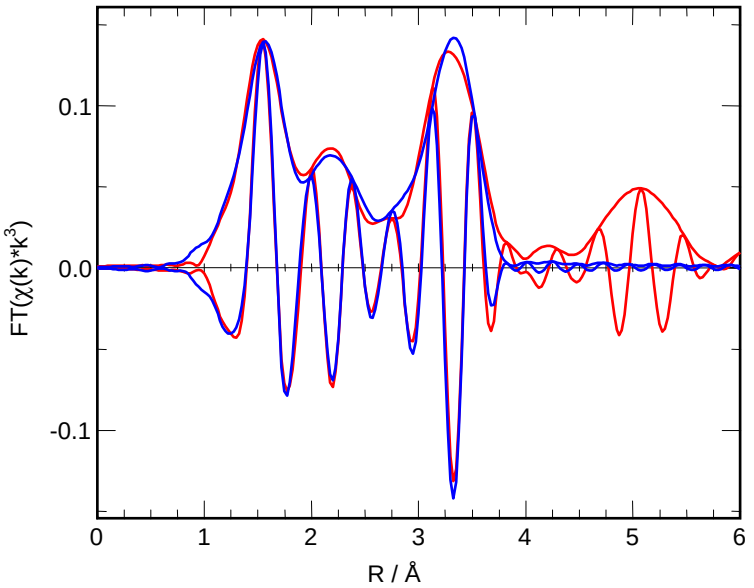
Acceptable variation of residual (e.g. 95 %) can be changed in "*Fit Options*".

ii) Molybdenum dioxide, MoO_2, Mo K edge,

theoretical phases and amplitudes calculated with FEFF 7.

(R range 1.0 - 4.0 Å, k range 2.2 - 15.5 $Å^{-1}$, N_{ind} = 27, N_{free} =11)

(Only single scattering paths (8) considered, MS paths omitted for clarity.)



Results of first try to refine MoO_2 model structure to XAFS data.

(*R model* corresponds to *crystallographic distances*)

Pair	CN	R, model	R	sig^2	E0
Mo-O	2	1.97	1.93	0.000393	-2.75
Mo-O	2	1.99	1.998	0.000393	-2.75
Mo-O	2	2.07	2.059	0.000393	-2.75
Mo-Mo	1	2.51	2.518	0.00305	-2.75
Mo-Mo	1	3.11	3.117	0.00305	-2.75
Mo-Mo	4	3.68	3.655	0.00305	-2.75
Mo-Mo	2	3.71	3.736	0.00305	-2.75
Mo-Mo	2	3.79	3.735	0.00305	-2.75

Issues:

* significance of free running Mo – O distances in first (slightly distorted) shell and confidence limits
* significance of free running E_0 in refinement and confidence limits
* reliable σ^2 parameters of Mo-O and Mo-Mo paths

(* significance of independent σ^2 parameters of various Mo-O paths, for instance) (not shown)

a) First try:

(all three Mo-O paths running free, all Mo-Mo paths free, single E_0 for all paths, one σ^2 for Mo-O paths, and one σ^2 for Mo-Mo paths, CN fixed, S_0^2 fixed)

```
-- Automated F-test for current fitting parameters -  Original R value:  7.915
 Par #03:   1.93          - F 0.52 , R:  8.167 (R: 7.915, Par: 1.9686   , Var: 2   %)  : maybe dependent
 Par #04:   0.00039261    - F 0.72 , R:  8.284 (R: 7.915, Par: 0.00062819, Var: 60  %)  : maybe dependent
 Par #05:  -2.7517        - F 0.47 , R:  8.491 (R: 7.915, Par:-3.302    , Var: 20  %)  : largely independent
 Par #07:   1.9983        - F 0.74 , R:  8.016 (R: 7.915, Par: 2.0383   , Var: 2   %)  : maybe dependent
 Par #11:   2.0589        - F 0    , R:  9.298 (R: 7.915, Par: 2.1001   , Var: 2   %)  : independent
 Par #15:   3.1166        - F 0    , R:  11.5  (R: 7.915, Par: 3.1789   , Var: 2   %)  : independent
 Par #16:   0.0030543     - F 0    , R:  10.87 (R: 7.915, Par: 0.0036652, Var: 20  %)  : independent
 Par #19:   2.5182        - F 0    , R:  14.15 (R: 7.915, Par: 2.5686   , Var: 2   %)  : independent
 Par #23:   3.6554        - F 0    , R:  9.758 (R: 7.915, Par: 3.7285   , Var: 2   %)  : independent
 Par #27:   3.7363        - F 0    , R:  8.304 (R: 7.915, Par: 3.8111   , Var: 2   %)  : independent
 Par #31:   3.7355        - F 0    , R:  8.29  (R: 7.915, Par: 3.8102   , Var: 2   %)  : independent

 -- Confidence limits of current fitting parameters -  Variation of residual within 95 %
 Par #03:   1.930005        +-  0.0969
 Par #04:   0.0003926089    +-  0.000253
 Par #05:  -2.751671        +- -0.48
 Par #07:   1.998318        +-  0.054
 Par #11:   2.058897        +-  0.0133
 Par #15:   3.116577        +-  0.00895
 Par #16:   0.003054334     +-  0.000128
 Par #19:   2.518219        +-  0.00574
 Par #23:   3.655393        +-  0.0141
 Par #27:   3.736336        +-  0.0327
 Par #31:   3.735466        +-  0.0328
```

* High F test parameters and high confidence limits are obtained for three independent Mo-O distances and E_0 parameters. Independent parameters are not significant and unreliable. Apparently, they need to be fixed or constrained in refinement.
* Mo-Mo paths appear mostly reliable with acceptable confidence limits. Mo-Mo paths at ~ 3.7 Å may be uncertain.

b) Second try:

(two independent Mo-O paths, all Mo-Mo paths free, single E_0 for all paths, one σ^2 for Mo-O paths, and one σ^2 for Mo-Mo paths, CN fixed, S_0^2 fixed)

```
-- Automated F-test for current fitting parameters -  Original R value:  8.085
 Par #03:   2.0171       - F 0    , R:  12.15 (R: 8.085, Par: 2.039    , Var: 2   %)  : independent
 Par #04:   0.0022393    - F 0    , R:  15.11 (R: 8.085, Par: 0.0043697, Var: 20  %)  : independent
 Par #05:  -3.2199       - F 0.32 , R:  8.691 (R: 8.086, Par:-3.696    , Var: 20  %)  : largely independent
 Par #11:   1.9398       - F 0.54 , R:  8.392 (R: 8.183, Par: 2.0628   , Var: 4   %)  : maybe dependent
 Par #15:   3.1154       - F 0    , R:  12.56 (R: 8.085, Par: 3.178    , Var: 2   %)  : independent
 Par #16:   0.0030204    - F 0    , R:  11.04 (R: 8.085, Par: 0.0036089, Var: 20  %)  : independent
 Par #19:   2.5169       - F 0    , R:  14.95 (R: 8.085, Par: 2.567    , Var: 2   %)  : independent
 Par #23:   3.6534       - F 0    , R:  8.884 (R: 8.084, Par: 3.7268   , Var: 2   %)  : independent
 Par #27:   3.7345       - F 0    , R:  9.202 (R: 8.086, Par: 3.8098   , Var: 2   %)  : independent
 Par #31:   3.734        - F 0    , R:  9.206 (R: 8.085, Par: 3.8094   , Var: 2   %)  : independent

 -- Confidence limits of current fitting parameters - Variation of residual within 95 %
 Par #03:   2.017069       +-  0.00352
 Par #04:   0.002239207    +-  0.000206
 Par #05:  -3.219888       +- -0.462
 Par #11:   1.939823       +-  0.102
 Par #15:   3.115384       +-  0.00927
 Par #16:   0.003020411    +-  0.000131
 Par #19:   2.516909       +-  0.0055
 Par #23:   3.65338        +-  0.0476
 Par #27:   3.734497       +-  0.026
 Par #31:   3.73404        +-  0.0259
```

* Considerable F test parameters and high confidence limits are also obtained for two independent Mo-O distances and E_0 parameters. Parameters are still not significant and unreliable. Apparently, they need to be further fixed or constrained in refinement.
* Mo-Mo paths appear mostly reliable with acceptable confidence limits. Mo-Mo paths at ~ 3.7 Å may be uncertain.

c) Third try:

(one independent Mo-O paths, all Mo-Mo paths free, E_0 set to zero and fixed, one σ^2 for Mo-O paths, and one σ^2 for Mo-Mo paths, CN fixed, S_0^2 fixed)

```
-- Automated F-test for current fitting parameters - Original R value:  9.025
Par #03:   2.0029       - F 0    , R:  15.12 (R: 9.025, Par: 2.043    , Var: 2   %)  : independent
Par #04:   0.0038144    - F 0    , R:  10.53 (R: 9.025, Par: 0.0045772, Var: 20  %)  : independent
Par #15:   3.1219       - F 0    , R:  13.24 (R: 9.025, Par: 3.1843   , Var: 2   %)  : independent
Par #16:   0.0030157    - F 0    , R:  11.12 (R: 9.025, Par: 0.0036188, Var: 20  %)  : independent
Par #19:   2.5242       - F 0    , R:  15.33 (R: 9.011, Par: 2.5747   , Var: 2   %)  : independent
Par #23:   3.6794       - F 0    , R:  9.297 (R: 9.011, Par: 3.753    , Var: 2   %)  : independent
Par #27:   3.7134       - F 0    , R:  9.904 (R: 9.025, Par: 3.862    , Var: 4   %)  : independent
Par #31:   3.7873       - F 0    , R:  9.869 (R: 9.025, Par: 3.863    , Var: 2   %)  : independent
```

Pair	CN	R, model	R	sig^2	E0
Mo-O	2	1.97	2.00	0.00381	0
Mo-O	2	1.99	2.00	0.00381	0
Mo-O	2	2.07	2.00	0.00381	0
Mo-Mo	1	2.51	2.52	0.00302	0
Mo-Mo	1	3.11	3.12	0.00302	0
Mo-Mo	4	3.68	3.68	0.00302	0
Mo-Mo	2	3.71	3.71	0.00302	0
Mo-Mo	2	3.79	3.79	0.00302	0

```
-- Confidence limits of current fitting parameters -
Variation of residual within 95 %
 Par #03:   2.002916       +-  0.0039
 Par #04:   0.003814353    +-  0.000243
 Par #15:   3.12187        +-  0.00989
 Par #16:   0.003015651    +-  0.000151
 Par #19:   2.524178       +-  0.0054
 Par #23:   3.679366       +-  0.0236
 Par #27:   3.713439       +-  0.0167
 Par #31:   3.787251       +-  0.0152
```

* All parameters independent with acceptable confidence limits. Notice the much improved Mo-Mo at ~ 3.7 Å and the good agreement with the model structure. Alternatively, instead of varying the distances of the Mo-O paths the same, the ΔR values with respect to the crystallographic distances could be varied the same (→ indeed slight improvement of residual).