Avoiding Some Pitfalls in XAFS Analysis

I Pitfalls

a. Wrong model

b. Wrong values because of correlations

c. Underestimate of uncertainties because of neglect of systematic errors

II Wrong Model

Good fit: $R^2 = \frac{\sum_i |\chi_i^e - \chi_i^f|^2}{\sum_i |\chi_i^e|^2} \lesssim 0.01$

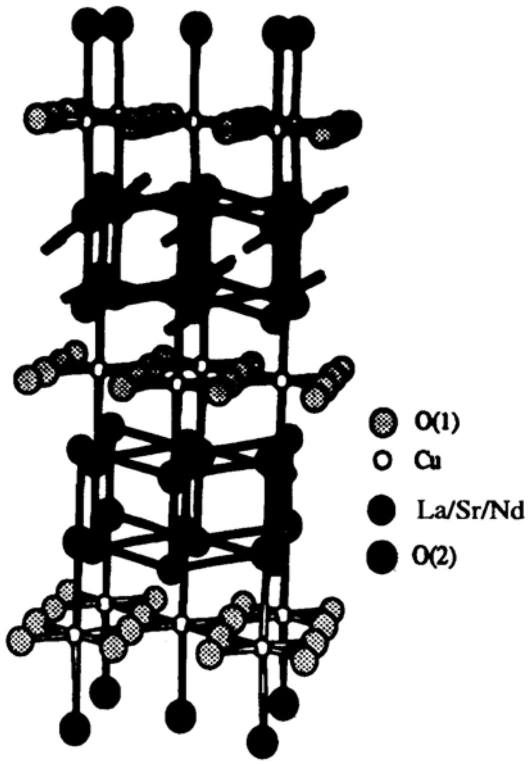
Not guarantee of good model

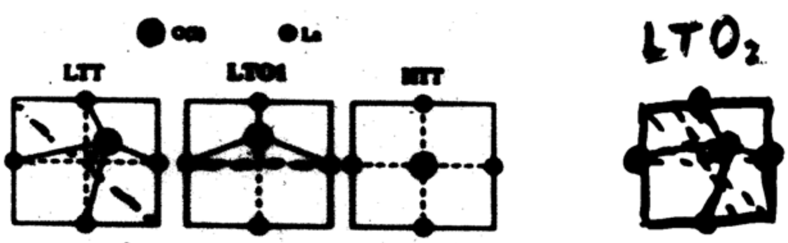
May be in local minimum with wrong model

Resulting model must give physical results:

1. $\sigma^2 > 0$

T dependence should fit Einstein or correlated Debye model, unless physical reason why not, e.g., phase transition





2 different distances

3 diff. distances

4 equal distances

4 different distances

	R^2	ν	χ^2/ν	$\sigma^2(O(2))$ [La-O(2)] $Å^2$	$\sigma^2(O(1))$
LTT	0.005	10	9	0.029(23)	0.002(3)
LTO_1	0.018	10	20	0.015(7)	0.006(.4)
$\boxed{LTO_2}$	0.014	10	15	0.002(1.5)	0.004(.4)
LTT + LTO_1	0.005	9	5.4	0.013(3)	0.000(.4)

Fits for

$La_{2-x-y}Nd_ySr_xCuO_4$

$x = 0.12$

$y = 0.40$

Red flag! claim that a distance is split, but results in $\sigma^2 < 0$.

If distance not split, $\sigma^2 > 0$.

2. Limit on spatial resolution of splitting

XAFS cannot not resolve splitting

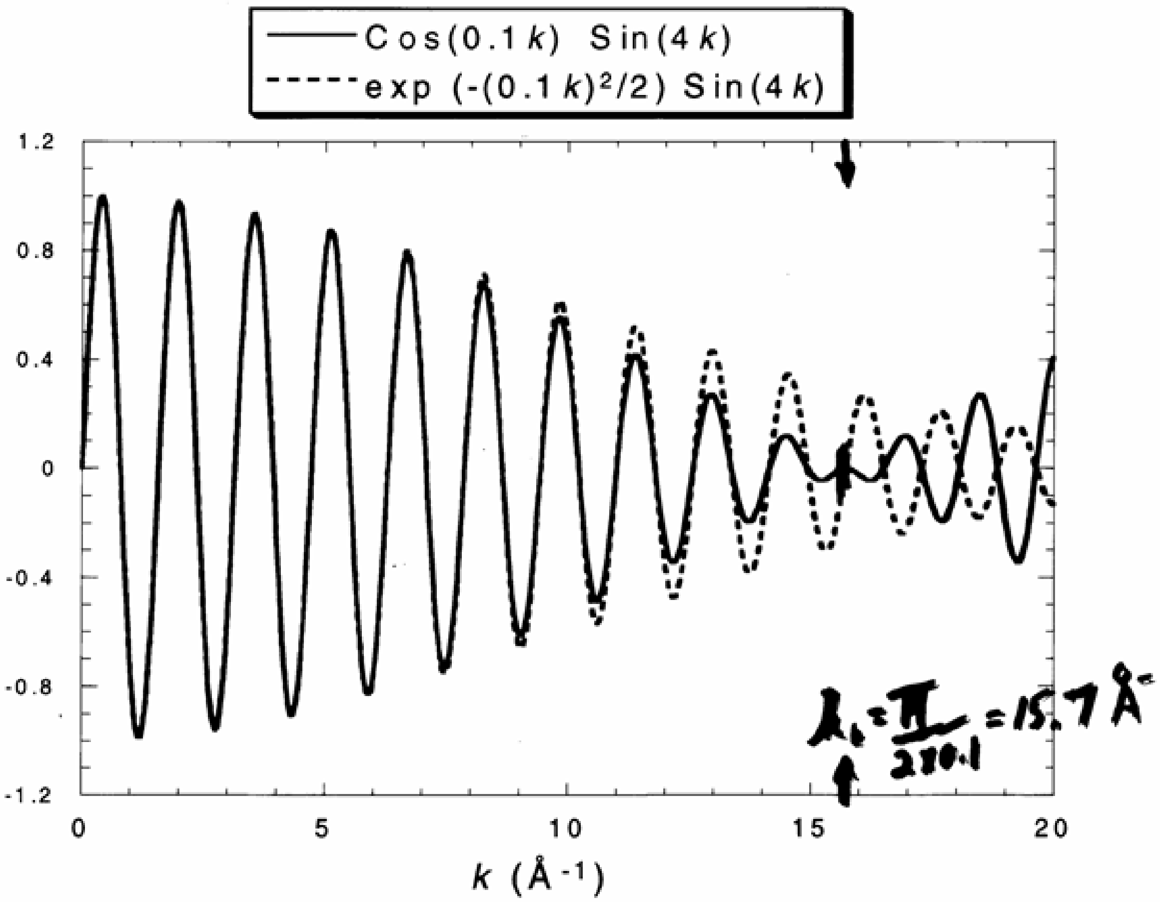
$$\Delta R < \frac{\pi}{2 k_{max}} \qquad \left(\text{beat occurs at } k_b = \frac{\pi}{2\Delta R} \right)$$

The difference between a gaussian disorder σ^2 and $\left(\frac{\Delta R}{2}\right)^2$ cannot be

resolved unless a beat can be detected.

3. $r_{12} >$ min. $\Rightarrow$ hard core distances

4. $|E_0| \lesssim 6\,eV$



Cos(0.1 k) Sin(4 k)
exp (-(0.1 k)²/2) Sin(4 k)
1.2
0.8
0.4
0
-0.4
-0.8
-1.2
0
5
10
15
20
k (Å -1)
λ₁ = π / 2×0.1 = 15.7 Å⁻¹

III Wrong structural values because of correlations

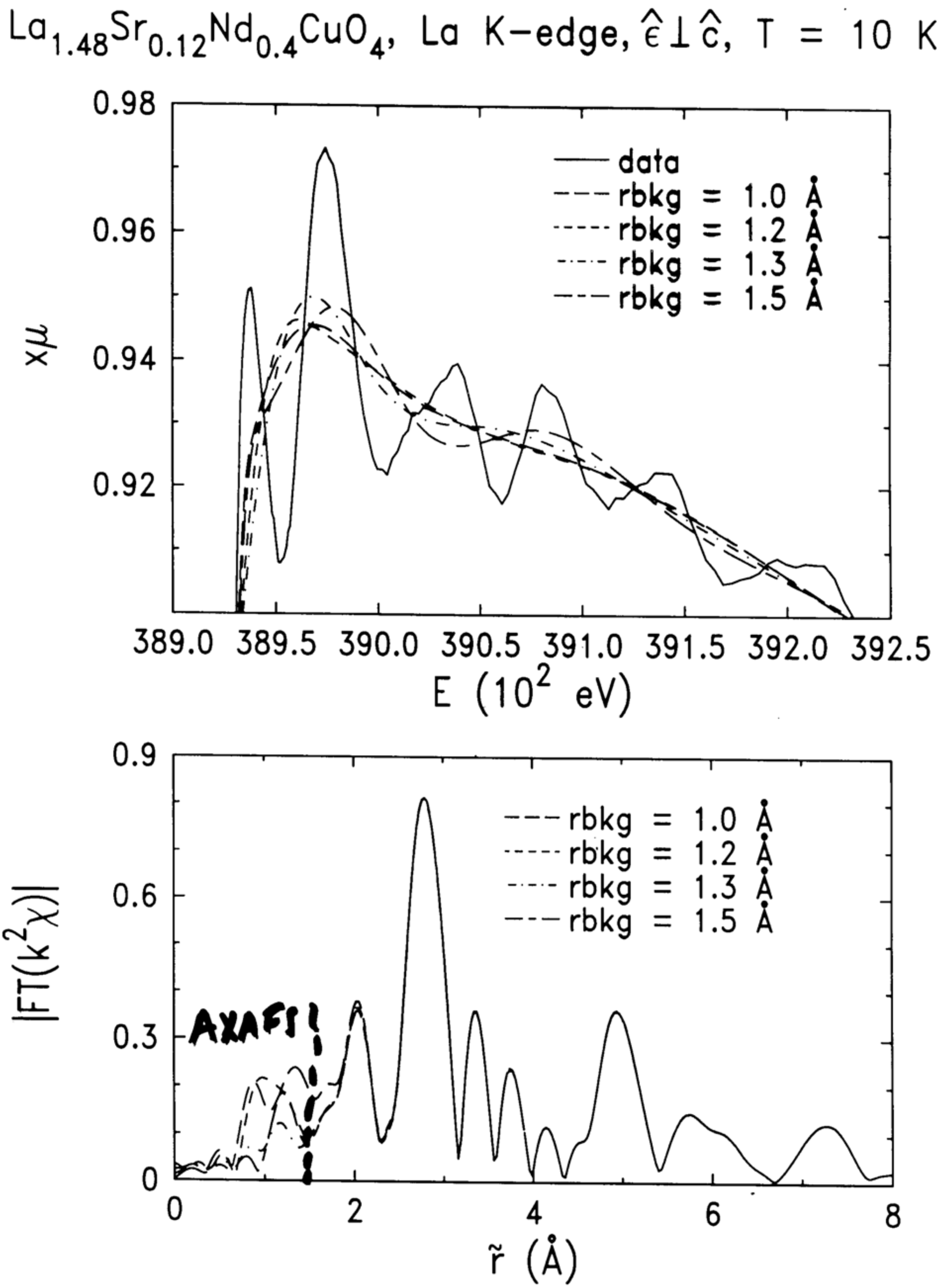
1. Correlation between background and signal.

For energies 50 eV and greater above edge it is straightforward to separate background and signal.

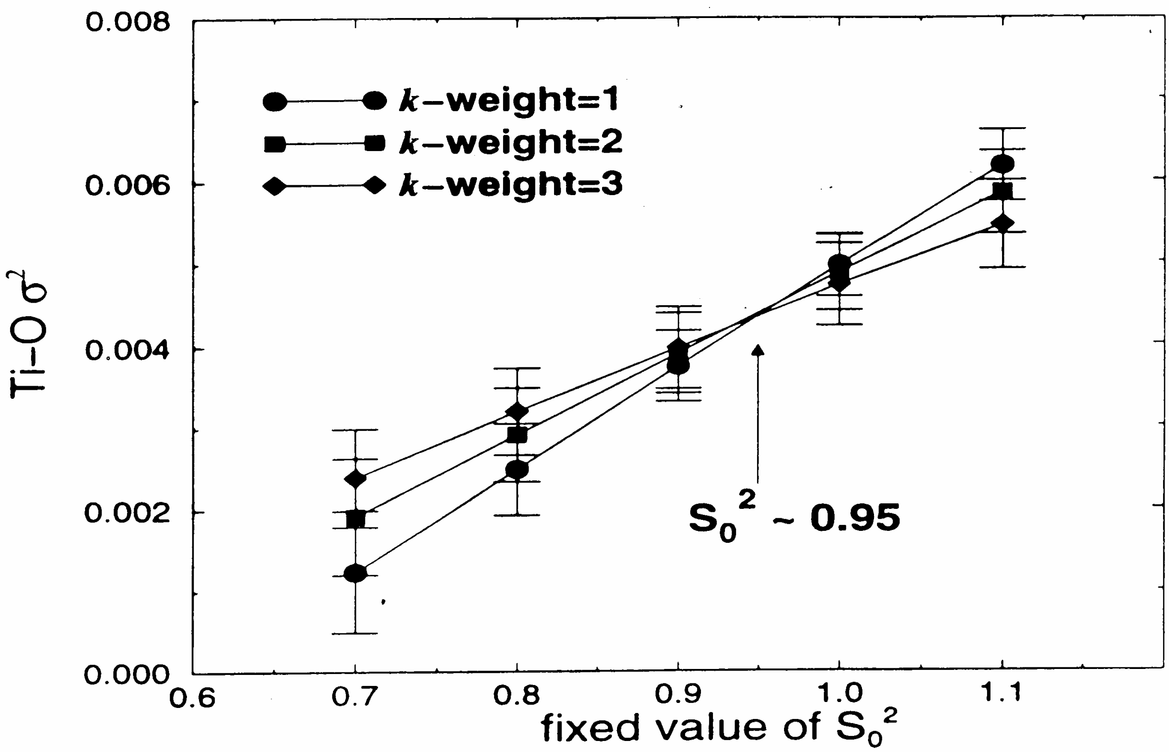
However, near edge the separation is not always obvious, especially when white line is present (examples)

Atomic XAFS (AXAFS) has been introduced to monitor changes in the charge distribution at the absorbing atom. Produces signal in $\chi(R)$ at $R < R_1$.

Absolute determination of AXAFS suspect. Relative changes (small) probably significant.



La1.48Sr0.12Nd0.4CuO4, La K-edge, ε̂ ⊥ ĉ, T = 10 K
data
rbkg = 1.0 Å
rbkg = 1.2 Å
rbkg = 1.3 Å
rbkg = 1.5 Å
xμ
0.98
0.96
0.94
0.92
389.0
389.5
390.0
390.5
391.0
391.5
392.0
392.5
E (10^2 eV)
rbkg = 1.0 Å
rbkg = 1.2 Å
rbkg = 1.3 Å
rbkg = 1.5 Å
|FT(k^2χ)|
0.9
0.6
0.3
0
AXAFS!
0
2
4
6
8
r̃ (Å)



0.008
0.006
0.004
0.002
0.000
0.6
0.7
0.8
0.9
1.0
1.1
k-weight=1
k-weight=2
k-weight=3
Ti-O σ²
S₀² ~ 0.95
fixed value of S₀²

2. Correlation between σ^2 and (N, S_0^2)

Can separate out the correlation by k^w, σ^2, S_0^2 plots or by T dependence. S_0^2 independent of T.

IV Neglect of Systematic Noise Pitfall.

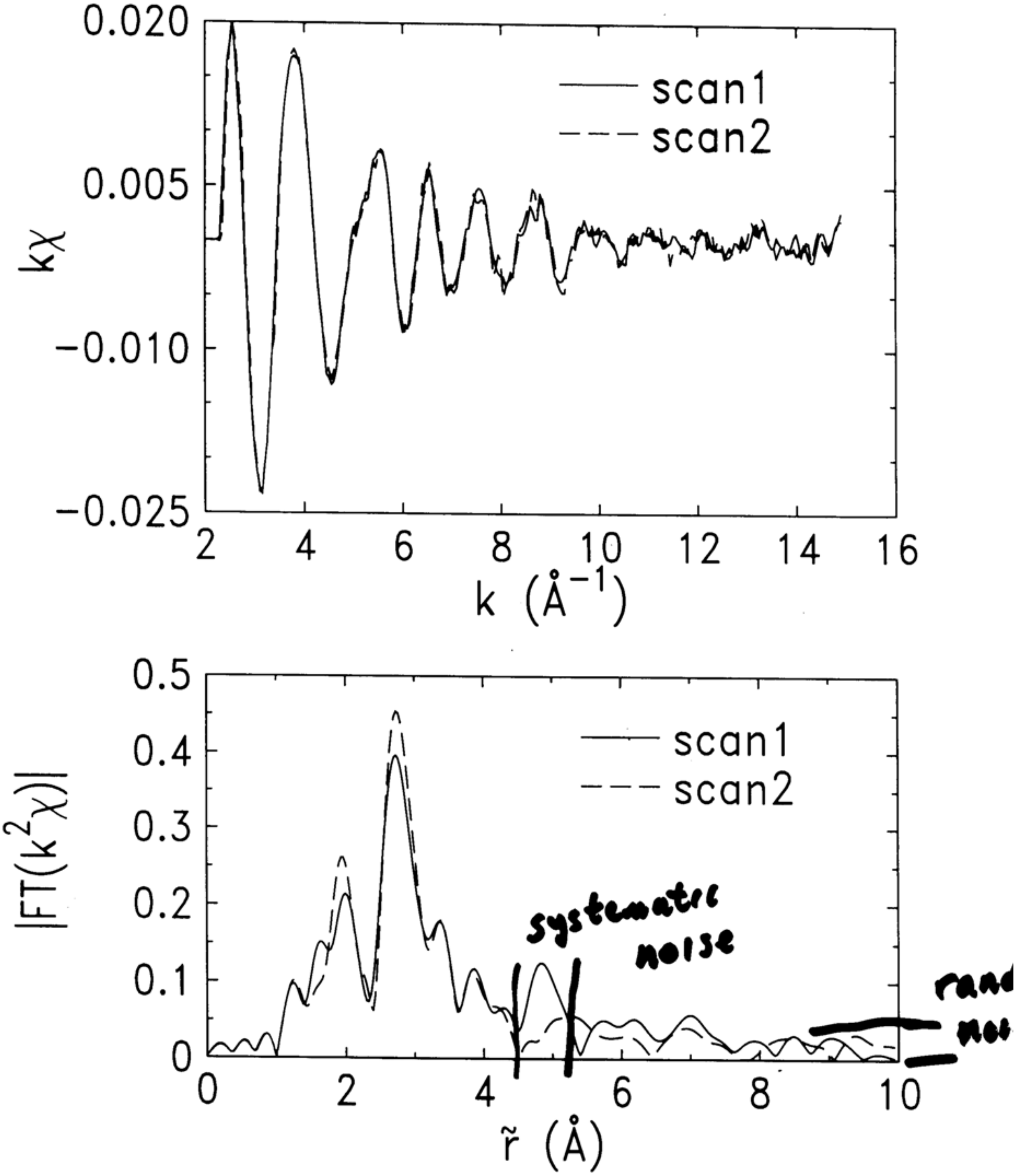
1. To detect systematic and random noise should take more than one scan for given physical conditions.

Can distinguish systematic noise like glitches in k-space

More subtle systematic noise may show up in R-space.

If random noise then should be constant as fn. of R.

$La_{1.48}Sr_{0.12}Nd_{0.4}CuO_4$, La K-edge, $\hat{\epsilon}\perp\hat{c}$, T = 300 K



2. Error Analysis - Systematic Errors

Systematic noise introduced by

Data analysis

a. Background Subtraction

b. F.T. windowing

c. Theoretical Standards

Systematic error introduced by measurement

a. item 1. (glitches, R-dependent noise)

b. Poor sample preparation

Thickness effect

Sample not what assumed because of deterioration, contamination, etc.

Error analysis Method can detect (some) systematic errors if done correctly.

Systematic errors dominate in most cases except for dilute samples!!

3. Estimate of Systematic errors using Error Analysis

All statistical methods for determinating errors do <u>not</u> work for systematic errors. It is this property that allows the estimate of systematic errors!
e.g., Systematic noise does not average to zero.

The trick is to determine the "statistical uncertainty" in the data by calculating difference in separate scans or by calculating $\chi(R)$ noise for large $\gtrsim 12 Å$. Use standard statistics methods such as reduced χ_ν^2 to find its value when normalized by ν (degrees of freedom)
If no systematic noise then $\chi_\nu^2 \approx 1$.
If not, then two possibilities:

$\nu = N_I - P$

N_I = information content

P = no. of parameters

$$N_I = \frac{2\Delta k\,\Delta R}{\pi} + 2\ (1)$$

N_I = no. of independent points in data, not no. of measuring points.

$$\frac{1}{2}\left[\sin(4.05k) + \sin(3.95k)\right]$$

$$A_1 \sin(2R_1 k) + A_2 \sin(2R_2 k)$$

$$N_I = A_1, A_2, R_1, R_2 = 4$$

(a) Wrong model assumed

(b) Systematic errors present

If $R^2 \lesssim 0.01$ then (a) probably not the case assuming model has physical results.

Can give estimate of systematic errors by multiplying errors determined from χ^2_ν analysis ε_r (statistics) by χ_ν, i.e. $\varepsilon_{rms} = \chi_\nu \varepsilon_r$.

Typically, concentrated samples, $\chi_\nu \approx 10$, so important correction. e.g., $\Delta\sigma^2 \approx 0.002$ not 0.0002 Å^2 for oxygen.

Reference: 1. IXS error analysis report April 2000

2. UWXAFS, FEFFIT documentation

V Summary

Researcher should be most critical assessor of his conclusions of his XAFS analysis.

Does his model pass test of being the correct one.

1. Good fit, $R^2 \lesssim 0.01$
2. physically correct.
3. Correlations between quantities correctly assessed and minimized when possible.
4. Have systematic uncertainties been accounted for in assessing errors?

Be conscientious and don't under-estimate errors!