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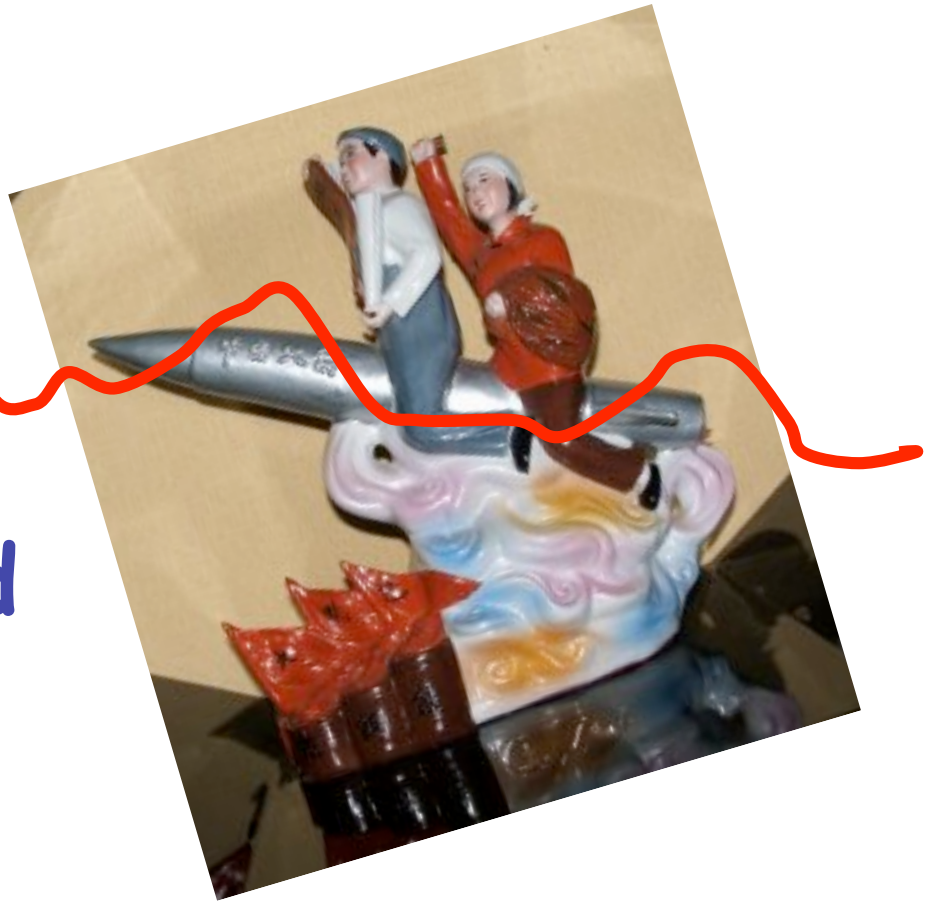
EXAFS is not a Black Box or How I Learned to Stop Worrying and Love the Fit



Scott Calvin

Sarah Lawrence College

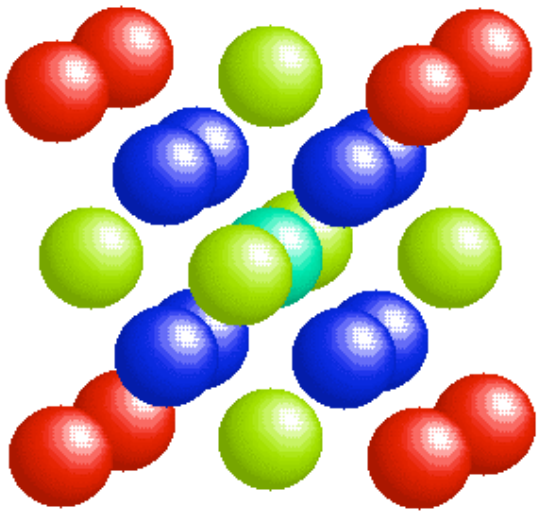
Why EXAFS is not a Black Box

Data →

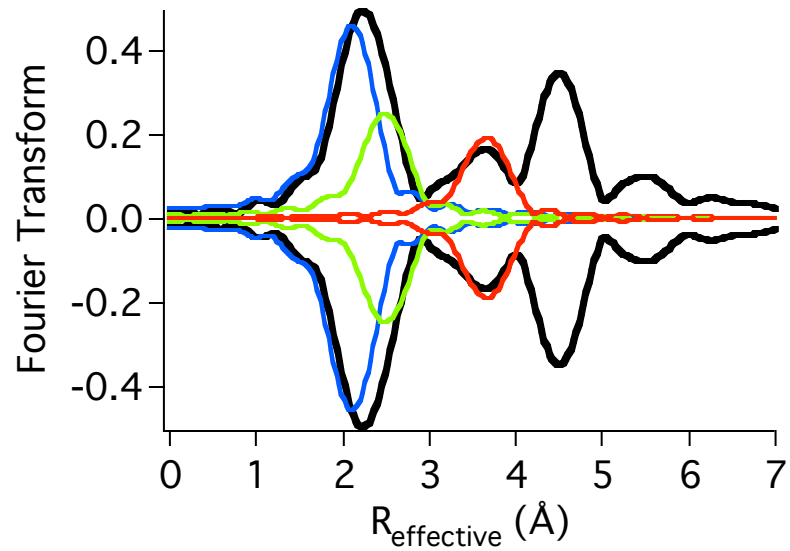
→ Structure

Reason #1: The Inverse Problem

This is "easy":



Structure

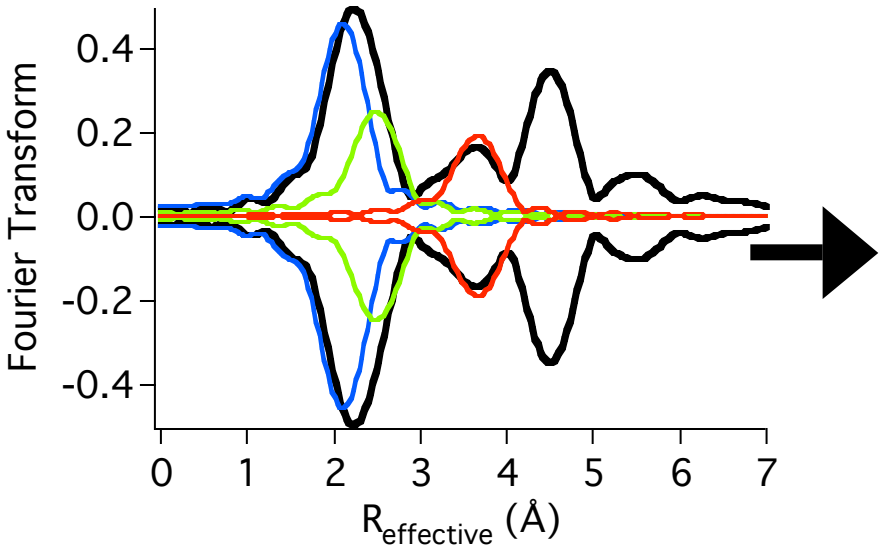


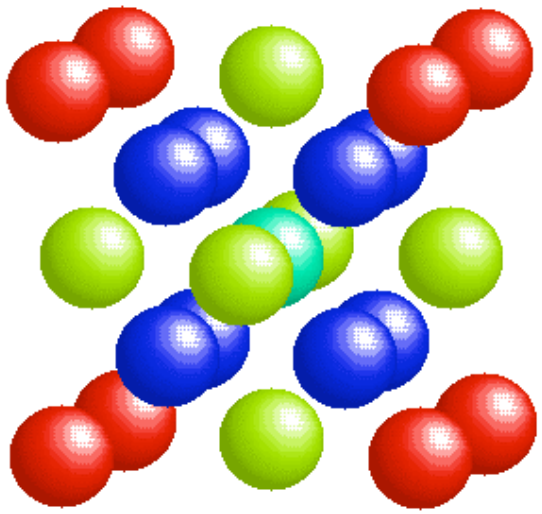
Fourier Transform of EXAFS

It's what FEFF does.

Reason #1: The Inverse Problem

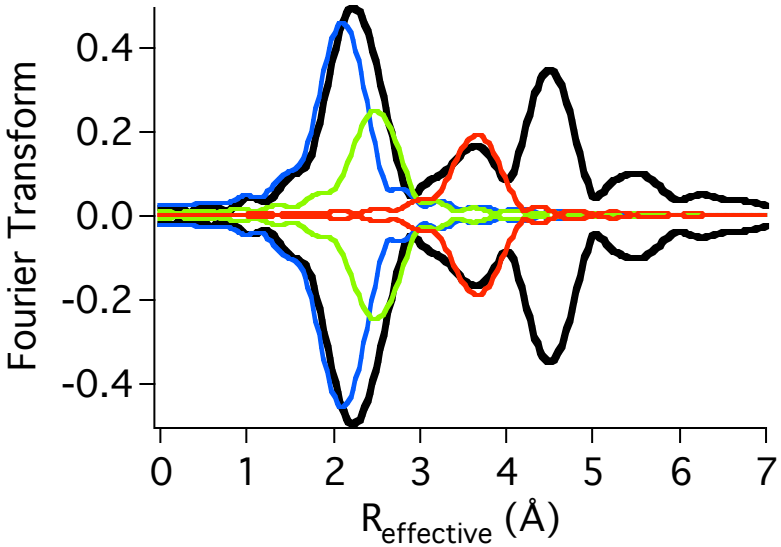
This is "hard":





What Makes it Hard?

- The peaks of the Fourier Transform are shifted down from the actual absorber-scatterer distances, typically by 0.3 to 0.5 angstroms.
- Multiple-scattering paths may be significant
- **More than one structure may correspond to the same spectrum!**



In a sense, the task is not just hard, it is impossible!

How to do the Impossible: Cheat!

- Make an **educated guess** as to the structure, then use FEFF to run the forward problem.
- Allow a computer program (e.g. IFEFFIT) to make a limited number of small adjustments to the guessed structure to optimize the fit with the data
- If a good fit cannot be found, the guessed structure is wrong. Try another guess.

The EXAFS Equation

$$\chi(k) = \sum_j \frac{S_0^2 N_j f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{k R_j^2} \sin[2kR_j + \delta_j(k)]$$

For each scattering path *j* (single and multiple), IFEFFIT can be told to optimize the following parameters:

- $S_0^2 N_j$ (primarily to fit coordination numbers)
- R_j (in practice, ΔR_j), the difference between the fitted R_j and the initial structure
- σ^2_j, the variance in the absorber-scatterer distance
- ΔE_o, a difference in the energy origin of the photoelectron from whatever was assumed during data reduction

Example: FeO

For FeO, FEFF generates the following list of paths out to a distance of 5 angstroms:

#	Deg.	Reff	amp.	fs	Scattering Path
1	6	2.163	100.00		[+] O_1 [+]
2	12	3.059	89.68		[+] Fe_1 [+]
3	24	3.692	13.76		[+] O_1 O_1 [+]
4	48	3.692	19.66		[+] Fe_1 O_1 [+]
5	8	3.746	34.69		[+] O_2 [+]
6	6	4.326	19.37		[+] Fe_2 [+]
7	6	4.326	13.99		[+] O_1 O_1 [+]
8	12	4.326	47.58	1	[+] Fe_2 O_1 [+]
9	6	4.326	11.72	1	[+] O_1 [+] O_1 [+]
10	6	4.326	4.42		[+] O_1 [+] O_1 [+]
11	6	4.326	29.18	2	[+] O_1 Fe_2 O_1 [+]
12	24	4.326	7.14		[+] O_1 Fe_1 O_1 [+]
14	48	4.484	6.52		[+] Fe_1 O_1 [+]
15	48	4.484	20.86		[+] O_2 O_1 [+]
16	48	4.484	25.12		[+] O_2 Fe_1 [+]
17	48	4.588	7.49		[+] Fe_1 Fe_1 [+]
18	24	4.837	52.54		[+] O_3 [+]

Note that there are five single scattering paths, and a number of additional multiple scattering paths with significant amplitude

Since IFEFFIT can fit four parameters per path ($S_0^2 N_j$, ΔR_j, σ^2_j, and ΔE_o), that's 20 parameters for the single scattering paths alone. Include all the multiple scattering paths shown and the total balloons to 72 parameters. Does EXAFS really contain that much information?

Information Content of EXAFS

According to information theory, the maximum amount of information contained in an EXAFS Fourier transform is given by:

$$N \approx \frac{2\Delta k \Delta R}{\pi}$$

Where Δk is the range of data selected in k-space and ΔR is the range of the Fourier transform being fit.

For good (but not great) EXAFS data, Δk might typically be 10 $Å^{-1}$ and ΔR might be 4 Å, yielding about 25 independent points. So, including multiple scattering paths, we do not have enough information to independently vary every parameter in the FeO example on the previous page.

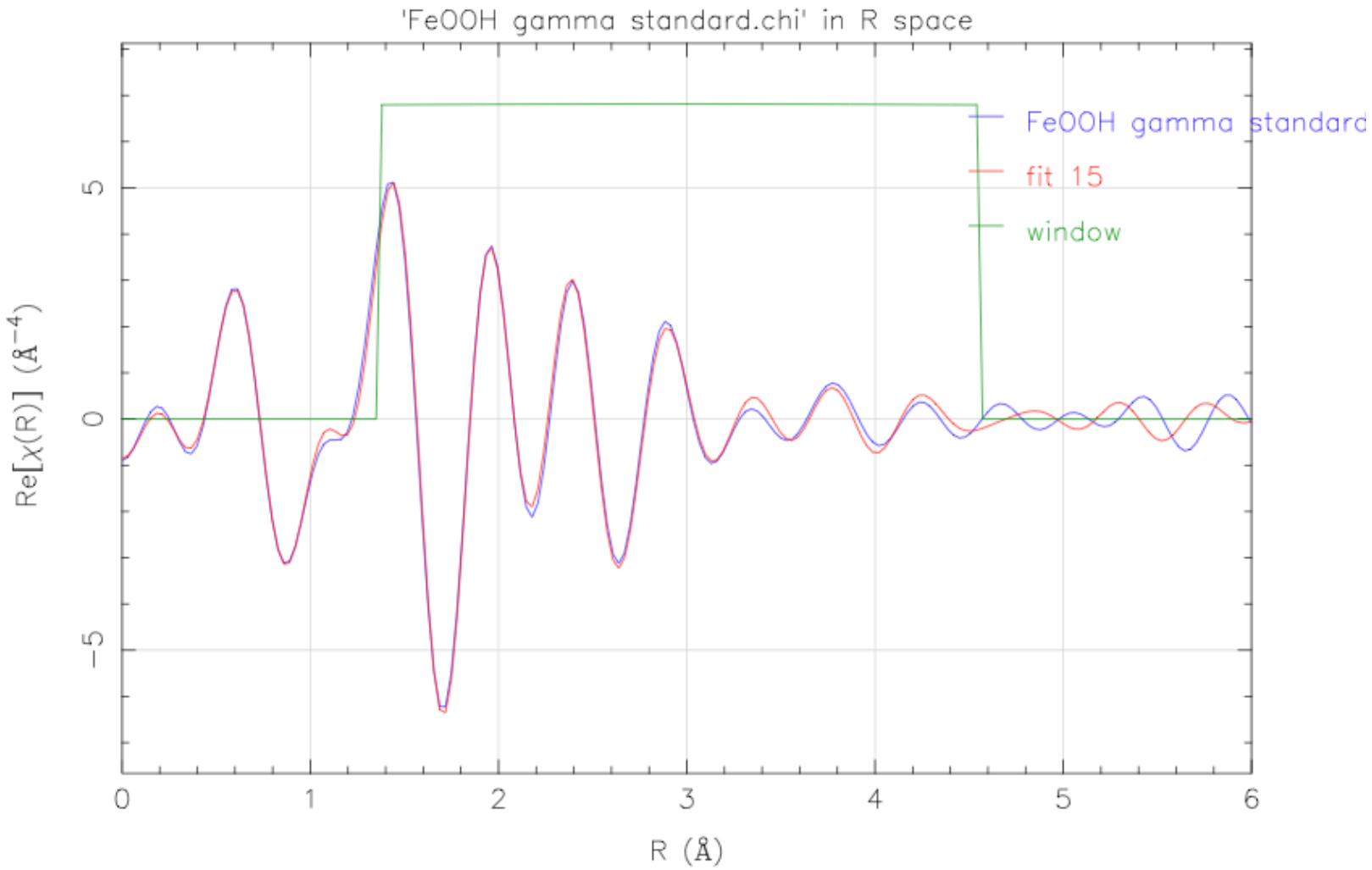
Information Content of EXAFS

It gets worse.

- The formula on the previous slide is actually the amount of information that could be extracted from an EXAFS Fourier transform if the spectrum were "ideally packed." They're not. So the actual amount of information is somewhat less.

- Remember: more than one structure can correspond to the same spectrum. If you try to vary a lot of parameters for relatively few paths, IFEFFIT may give you a fit that looks brilliant--but corresponds to some completely nonphysical structure.

An Example of a False Fit



The Solution: Science!

We're not mathematicians, and we're not data technicians. We're all scientists of one type or another. That means we have additional information about our system and our world. We can use that information to cut down on the number of parameters being fit.

IFEFFIT provides two ways to do this: **constraints** and **restraints**. Today we'll talk about constraints; restraints are a more advanced topic which we may discuss later.

A Very Simple Example of a Constraint

It seems plausible that the energy origin of the photoelectron does not depend on what the electron then scatters off of; i.e.

ΔE_o should be the same for every path.

If 18 paths are being fit, that reduces the number of free parameters by 17!

But How Do I Know A Constraint is Justified?

It has been argued, for instance, that it may actually help to use different ΔE_o's for different paths, perhaps as a way of compensating for approximations made by FEFF.

Using the software you are learning in this course, it is not difficult to try fits with and without a given constraint. If the constraint is not appropriate, the statistical quality of the fit (as measured by something called "reduced chi-squared"), should be significantly better without the constraint.

More Examples of Simple Constraints

- Perfect crystals: if a crystal is not defective, the coordination number for all paths may be known *a priori*
- Lattice expansion: for substances with high symmetry, it's possible that the sample differs from the model structure by a constant expansion factor
- Similar paths behave similarly: oxygen paths "a long way" from the absorbing atom may all have similar values of σ^2, for instance

More Complicated Constraints

IFEFFIT allows for fairly complicated mathematical expressions to be used as constraints. Just a few examples:

- Geometric: for example, an orthorhombic distortion will change the lengths of paths in fairly complicated but specific ways
- Thermal: known patterns of temperature dependence (e.g. Debye laws) may reduce the number of free parameters when data is collected as a function of temperature
- Doping: principles like Vegard's law may be helpful dealing with doped crystals
- Stoichiometry: if the chemical composition of a sample is known, it may sometimes be used to constrain average coordination numbers
- Size/morphology of nanomaterials can also be used to constrain average coordination numbers
- Almost any relationship between parameters that can be expressed mathematically can be used as a constraint!

Common Fitting Strategy #1

This one works well for substances which are expected to be fairly ordered and well known.

For instance, a material scientist might be investigating ferrite nanoparticles, with an interest in how they differ from the bulk.

- Start with a highly constrained model with a large ΔR.
- This allows a quick determination as to whether the sample is essentially "as advertised."
- Experiment with releasing constraints to probe possible differences from the model structure.

Common Fitting Strategy #2

This one works well for substances which do not correspond to known crystals.

- Start with nearest neighbor paths and relatively few constraints.
- As the structure becomes more clear, attempt to add reasonable constraints and perhaps more distant paths.

The Point of Fitting

Remember, you are trying to answer one or more questions about your sample by EXAFS. The fit is not an end in itself! It is often helpful to divide questions into two types:

- **Qualitative**. For example, "Is my sample Fe_2O_3?" Qualitative questions are often addressed by trying to fit different starting structures.

- **Quantitative**. For example, "What is the iron-oxygen bond length in my sample?" Or "What fraction of my sample is oxidized?" These questions are generally answered by allowing parameters you are interested in to by varied by IFEFFIT.

Do I Have a Good Fit?

Criterion 1: Statistical Quality

- Statistical quality of fit is measured by "reduced chi-square," χ_ν^2. Oddly, this is *not* related to $[\chi(k)]^2$…we're just out of symbols!

$$\chi_\nu^2 = \frac{1}{\text{degrees of freedom}} \sum_i \left(\frac{\text{difference between data and fit}_i}{\varepsilon_i} \right)^2$$

- ε_i is the uncertainty in measurement *i*. This quantity is difficult to estimate. IFEFFIT takes a shot at it by looking at noise high in the Fourier transform, but it's not necessarily a good estimate within the fitting range.

- If the difference between fit and measurement is entirely attributable to measurement uncertainty, then the reduced chi-square should be around 1.

- Unfortunately, because ε_i is difficult to estimate, the actual value of the reduced chi square is not very useful for judging the quality of the fit.

- It is very helpful, however, for comparing two fits on the same data set! For instance, if adding or removing a constraint causes the reduced chi-square to increase substantially, then it is probably not a good thing to do.

Do I Have a Good Fit?

Criterion 2: Closeness of Fit

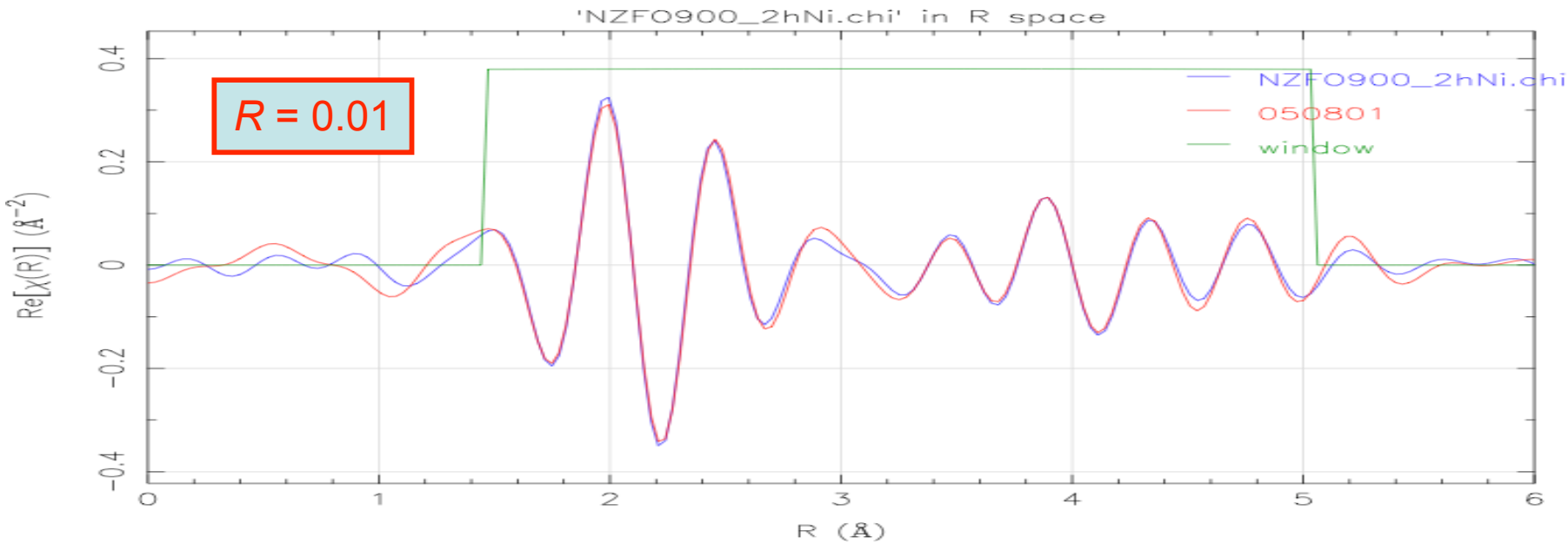
- This is not the same thing as a statistically good fit. If you have *really* good data, for instance, it can pick up very subtle variations between your constrained model and the sample. That can make your fit statistically poor. And yet the constrained model is "pretty good," even though the data would support better. To reflect this notion of closeness of fit, we use the EXAFS *R*-factor:

$$\mathscr{R} = \frac{\sum_i \left(\text{difference between data and fit}_i\right)^2}{\sum_i \left(\text{data}\right)^2}$$

- My off-the-record guidelines for interpreting the *R*-factor for data of moderate quality:

Range of *R*	Interpretation
< 0.02	Good enough
0.02-0.05	Either model has some details wrong, or data is low quality. Nevertheless, consistent with a broadly correct model.
0.05-0.10	Serious flaws in model or very low quality data.
> 0.10	Model may be fundamentally incorrect.

Do I Have a Good Fit?



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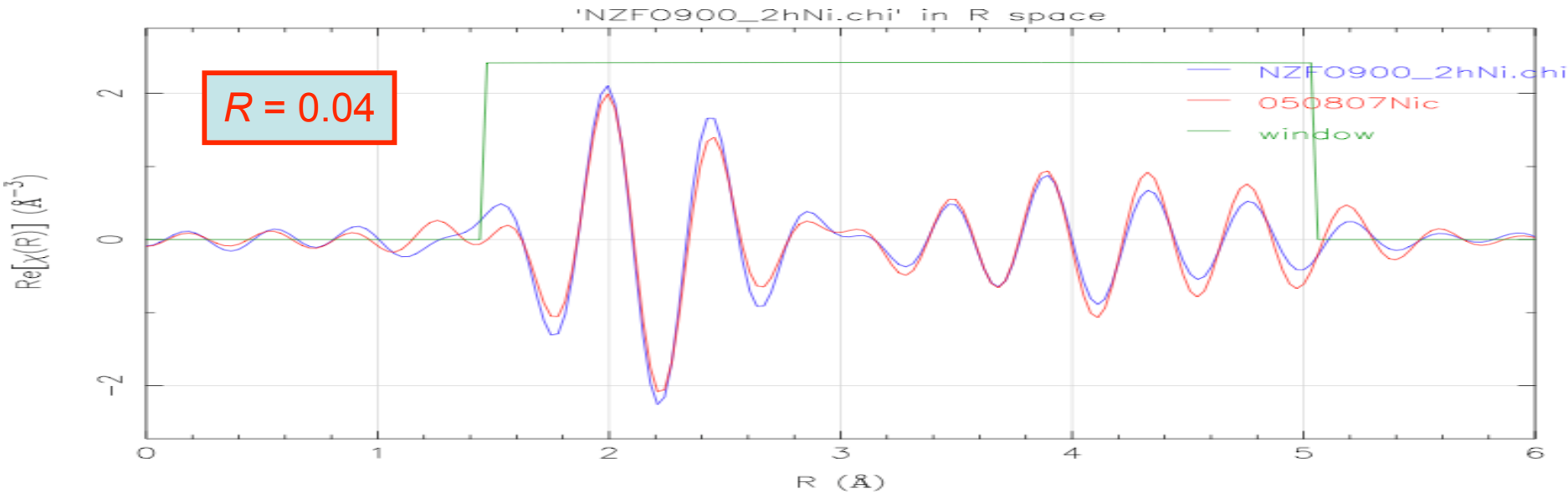

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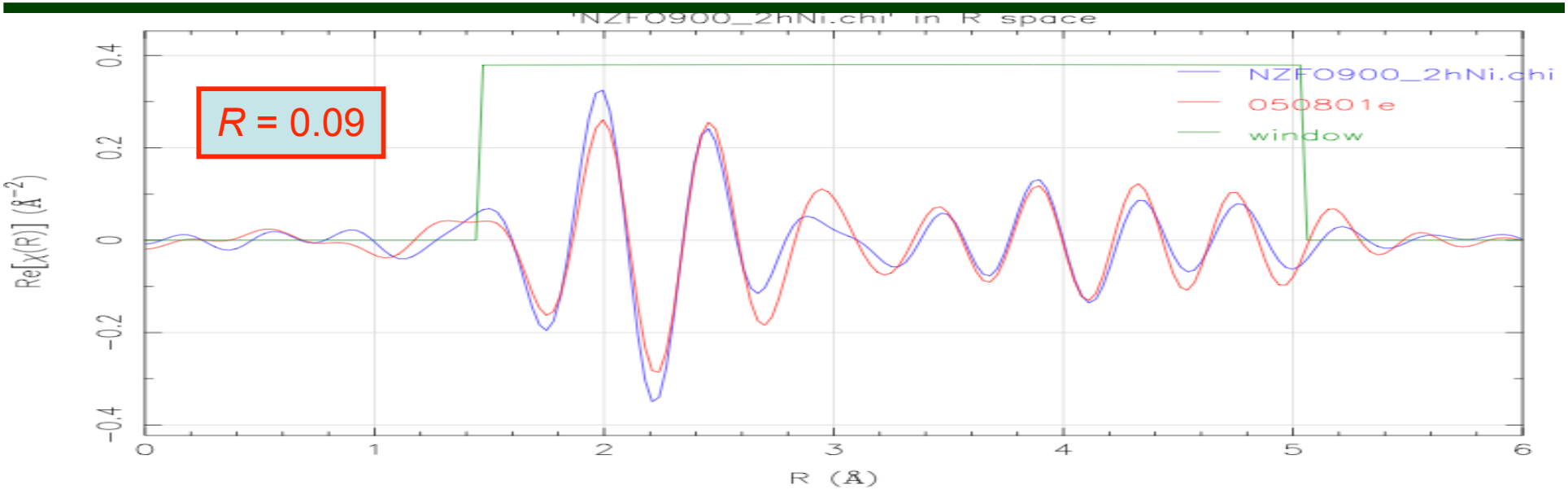

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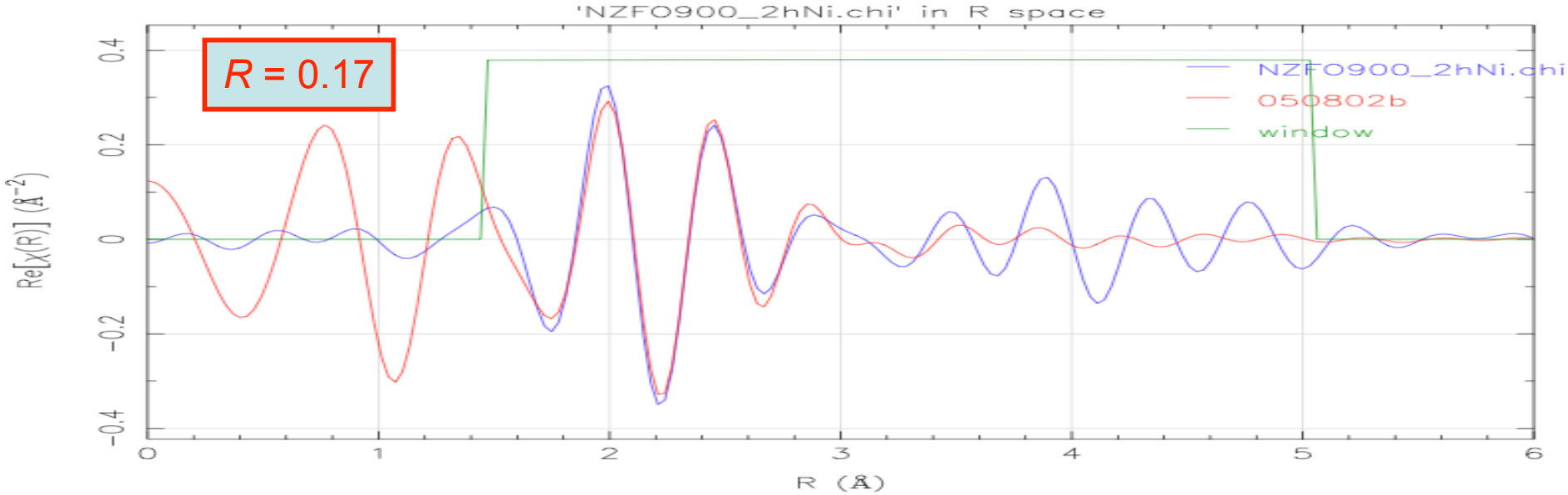

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Do I Have a Good Fit?

Criterion 3: Does it Make Sense?

- The danger of "false fits" means that IFEFFIT may generate a close match of fit to data that is utter nonsense. This can generally be detected by examining the values of parameters allowed to vary in the fitting process. False fits are often marked by one or more "unreasonable" values for parameters.

- "Isn't this a circular argument? Aren't you just rejecting fits that don't give you the results you want?" No, although care must be taken to guard against cherry-picking fits. The key is to reject fits that are physically highly implausible, not ones that support an alternative but plausible hypothesis. Typical examples of physically implausible parameters:

  - S_o^2 less than 0.50 or more than 1.20 (*should* be 0.80 to 1.0)
  - E_o not on or very near rising portion of the edge (more in a later talk in this workshop)
  - Unheard of bond lengths for the species involved
  - Negative values of σ^2
  - Excessive coordination numbers (e.g. 20)
  - Site occupancies negative or greater than one
  - Any parameter greatly at odds with a "known" value (probably determined by another experimental technique)

- "OK, so those fits are false. How do I know a false fit wouldn't happen to generate reasonable parameters?" It might, but it's less likely. It is a good idea, though, to "stress" your fit, which leads us to the next criterion…

Do I Have a Good Fit?

Criterion 4: Stability

- A good fit should be stable, meaning that the key results should not be sensitive to details of the fitting strategy.

- Always test the stability of your final fit by trying to "stress" it. That may be done in the following ways:

  - Change the *k*-range of data being used
  - Change the *R*-range of the Fourier transform being fit
  - Change the *k*-weight
  - Remove a constraint

- If the fit is good, modest changes in the above should not change the answer(s) to the scientific questions you are trying to address.

Do I Have a Good Fit?

Criterion 4: Stability (continued)

- The following often occur during stability checks, but are *not* cause to reject the initial fit:
  - Some of the stability checks yield very large uncertainties for some parameters
  - Parameters which are not of interest drift outside of their original uncertainties
  - When the details of the fitting strategy are changed sufficiently, the fit may get "lost" and replaced by a patently false fit
  - The *R*-factor degrades
- On the other hand, any of the following suggest more work needs to be done:
  - Parameters which answer your scientific questions drift outside of their original uncertainties without other indications that the fit has become "bad"
  - The fit flips to another set of values which also appear reasonable and with a comparable R-factor

Do I Have a Good Fit?

Criterion 5: Precision

A fit that tells you a bond length is 2.24 ± 1.45 angstroms doesn't tell you much about that bond length.

If it's something you're interested in, you'd like a fit with better precision.

Do I Have a Good Fit?

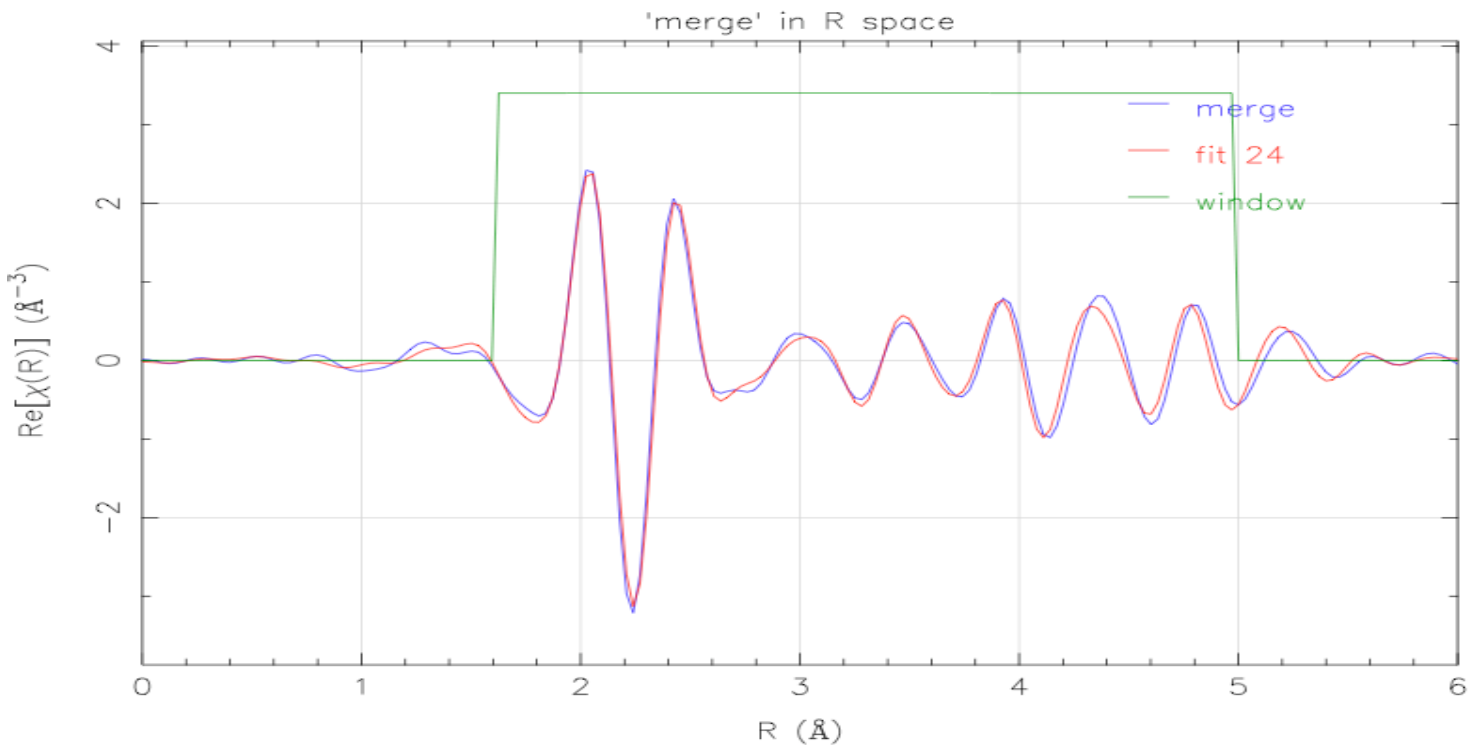
Criterion 6: More data is better

All else being equal, a fit which uses more of your data (a wider *k*-range and a wider *R*-range) is more convincing.

Do I Have a Good Fit?

Criterion 7: Agreement outside the fitted range

If the fit agrees with the data fairly well outside the range being fitted, that's a good sign.



Do I Have a Good Fit? Summary.

Criterion 1: Statistical quality
Criterion 2: Closeness of fit
Criterion 3: Sensible results
Criterion 4: Stability
Criterion 5: Precision
Criterion 6: More data is better
Criterion 7: Agreement outside the fitted range

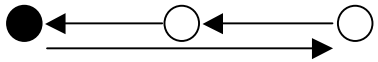
When Am I Done Fitting?

- Fitting almost always follows a pattern of diminishing returns; as the fit improves, the continued improvement gets smaller and smaller per hour you put in.
- Remember the initial purpose of your investigation. While more refined fits are always nice for publication, a question as to whether a sample is composed of a given compound generally demands less work than determining a second-nearest-neighbor bond length to 0.01 angstrom accuracy.

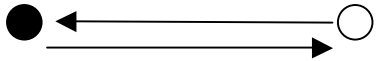
The Elephant in the Room: Multiple-Scattering Paths

You may be tempted to leave these paths out. But generally, a crudely constrained multiple-scattering path is more accurate than a missing one.

Some multiple-scattering paths can be constrained rigorously. For example, a "focused" path like:

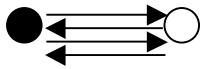


is the same as the corresponding single path:

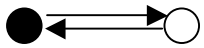


as far as the bond length and σ^2 are concerned.

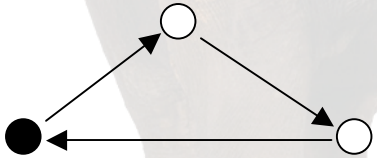
Similarly, this path:



Has twice the change in length and four times the σ^2 of the corresponding direct-scattering path:



But triangle paths are not so clear-cut:



The good news is that triangle paths usually make a relatively small contribution to the fit. A crude but usable way of constraining them will be shown during the demo.

Are Single-Shell Fits the Most Reliable?

No!

If you know something about scatterers beyond the nearest-neighbor, fitting only the first shell means you're throwing information away. Even if you're only interested in questions about the first shell, you'll get a more reliable fit if you can include more shells.

Fancy Fitting

We won't get to it today, but it's good to know about some additional things that can be done when fitting with IFEFFIT:

- **Restraints**. This forces a parameters to stay *near* a value while still allowing it to vary a bit. A special case is a "penalty" restraint, which forces a parameter to stay within a specified range.

- **Multiple data set fits**. Data from more than one sample,more than one edge of a given sample, or a sample under more than one set of conditions can be refined simultaneously. Why is this useful? Because some parameters may be the same for all data sets; for example, in a temperature series, the chemical composition might remain the same.

- **Multiple phases**. An element in a sample might be in more than one environment (for instance, metal and oxide). A FEFF calculation can be run for each phase and combined to make a fit. Doping and compounds with nonequivalent crystallographic sites are also handled in this way.