Improvements in modeling EXAFS with Many-Pole Self-Energy and FEFF8.5

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Abstract.
While theoretical standards such as those from FEFF have many advantages for EXAFS analysis, the quality of fit statistics and estimation of parameter uncertainties has always been somewhat problematic using them. Even though the calculations reproduce EXAFS features sufficiently well to give bond distances accurate to 0.01 Å or so, fits to high-quality experimental spectra will have fit residuals far larger than the experimental uncertainties. One of the possible causes for this mis-fit is from approximations made in the phenomenological calculations of the inelastic losses, though this has been difficult to test conclusively in the past. Recent improvements in calculations of inelastic losses using a many-pole self-energy (MPSE) using a real-space calculation of the dielectric function have been shown to give significant improvements in XANES calculations. Here, we discuss the use of MPSE calculations for EXAFS analysis, and show that these calculations from FEFF8.5 can quantitatively improve fit quality for EXAFS, reducing mis-fits by a factor of 2 or more compared to FEFF6. This approach may also allow the semi-physical fit parameter $S_0^2$ to be avoided. The implications for improving precision for EXAFS analysis and the nature of the remaining fit residual are discussed.

1. Introduction
The use of theoretical standards for EXAFS analysis has many advantages, including the ability to model complex distortions, three-body correlations, and multiple-scattering of the photo-electron, as well as avoiding difficulties of finding suitable experimental standards for arbitrary systems. However, it has been noted by Bridges[1] and others, that the ultimate precision of analysis with theoretical standards is generally worse than the most carefully constructed analyses with experimental standards. This is understandable since comparing two nearly identical experimental spectra can very accurately reveal subtle differences without accounting for the entire spectra, while in a comparison to a first-principles calculation, the calculation needs to account for all parts of the spectra with similar accuracy. Indeed, Pettifer et al showed[2] that a careful different EXAFS experiment can be sensitive to distance changes of 5 fm or less between samples in nearly identical conditions. This level of precision, which is 100 times better than that routinely achieved with EXAFS analysis, is due principally to two causes: 1) extremely reproducible energy values, and 2) an analysis that was not based on comparison to theoretical standards. Thus, while theoretical standards as from FEFF are now used widely for quantitative EXAFS analysis, there is clearly room for improvement in the ultimate precision to be gained in such analyses by understanding the sources of the absolute errors in these calculations.
Table 1. Parameters for fit to room temperature Cu foil using FEFF6.0. Fit ranges were \( k = [2, 16] \, \text{Å}^{-1} \), \( R = [1.65, 2.6] \, \text{Å} \), with the Fourier transform using \( k \)-weight=2.

| Fit Parameters and uncertainties: | \( R = 2.543(0.003) \, \text{Å} \) | \( \Delta E_0 = 4.1(0.5) \, \text{eV} \) | \( S_0^2 = 0.96(0.05) \) | \( \sigma^2 = 0.0085(0.0004) \, \text{Å}^2 \) |
|----------------------------------|---------------------------------|-----------------|-----------------|----------------|
| Goodness-of-Fit Statistics:     | \( \epsilon_k = 1.6 \times 10^{-4} \) | \( \chi^2 = 1012 \) | \( \chi^2_{\nu} = 242 \) | \( \mathcal{R} = 0.0016 \) |

When using a standard \( \chi^2 \) analysis to determine goodness-of-fit, the reduced chi-square statistic, \( \chi^2 = \chi^2/(N-N_{\text{carys}}) \) (for \( N = \Delta k \Delta R/\pi \) independent data points and \( N_{\text{carys}} \) variables) should be \( \approx 1 \) for a “good fit”, where

\[
\chi^2 = \frac{1}{\epsilon_k^2 N} \sum_{i} [\lambda_i^{\text{data}} - \lambda_i^{\text{model}}(\vec{x})]^2
\]

and \( \epsilon_k \) is the estimated noise in the data. With good data an realistic estimates of \( \epsilon_k \), values of \( \chi^2 > 50 \) are common when using models from FEFF. The magnitude of this mis-fit also gives large error bars for parameters estimated in a minimization procedure – the larger the absolute mis-fit, the larger the parameter uncertainties. The absolute errors are no doubt due to the approximations that go into the \textit{as initio} calculations.

Among the approximations which may have the largest impact on the mis-fit are those that go into describing intrinsic and extrinsic inelastic losses that typically are put into the mean-free-path \( \lambda(k) \), amplitude reduction factor \( S_0^2 \) or other excitation channels. Indeed, there has been some work over the past decade on these issues\cite{4}, but with limited quantitative improvement for EXAFS. In contrast, a great deal of work has been done to document and make ad-hoc models to account for multi-electron excitations in EXAFS\cite{5, 6}, which shows good evidence that the quantitative modeling of EXAFS requires an understanding of the electronic state of the excited atomic beyond the simple picture most often used in analytical treatments. In this paper, we explore the nature of the large mis-fit found when using theoretical standards, and show that using improved inelastic terms from FEFF8.5 with a many-pole self-energy (MPSE)\cite{7} for modeling EXAFS gives nearly a factor of 3 improvement compared to FEFF6 in the \( \chi^2 \) for Cu metal data.

2. Cu foil data room temperature: EXAFS and \( \epsilon_k \), the measurement uncertainty

We begin by modeling the first neighbor distance for Cu K-edge data of a room temperature Cu foil. Such data has been a model case for many analyses, and is often used as a demonstration of the EXAFS technique. The fit to this data with a FEFF6.0\cite{8} calculation gives a remarkably large mis-fit, with \( \chi^2 \approx 240 \). This fit, as all fits described in this paper, optimized \( R \), \( \sigma^2 \) (mean-square relative displacement), and \( E_0 \) (energy origin). The first shell coordination number \( N \) was set to 12 and the overall amplitude parameter \( S_0^2 \) was also optimized. The fit was done in \( R \)-space, over \( k \) and \( R \) ranges of \( k = [2, 16] \, \text{Å}^{-1} \), and \( R = [1.65, 2.6] \, \text{Å} \), with a \( k \)-weight=2. A simple model for the second shell and first-triangle paths was included to account for spectral leakage of higher shells into the first shell. No parameters for these further paths were optimized, as the fit was restricted to the first shell. Table 1 shows the fitted parameters and goodness-of-fit statistics for this simple fit, performed with IFEFFIT\cite{9}. The uncertainties listed do account for correlations between parameters, and are estimated to increase \( \chi^2 \) by \( \chi^2_{\nu} \).

As is typically obtained for good data, the uncertainty in \( E_0 \) is about 0.5 eV, the uncertainty in \( R \) is a bit less than 0.01 Å, and the amplitude factor \( S_0^2 \) is determined to about 5%. A plot of
Figure 1. (a) EXAFS $k^2\chi(k)$ for Cu foil at room temperature (solid) and a 2mM Zn nitrate solution (dashed). (b) The same data as $|\chi(R)|$ on a log-scale. From the range $R = [15, 25]$ Å, the $\epsilon$ for $\chi(k)$ is estimated to be $4.6 \times 10^{-4}$ for the Zn data and $1.6 \times 10^{-4}$ for the Cu data. The value for Cu is likely an overestimate, as this signal is above the noise level past 15 Å.

The best-fit model shows very good agreement with the data. Of course, the value for $\chi^2_{\nu}$ depends on the value of $\epsilon$, the estimated noise in the data. Earlier work[3] showed that estimating $\epsilon$ from the high-$R$ components ($R = [15, 25]$ Å) of the EXAFS spectra works well for fairly noisy data. For higher-quality data, the situation is somewhat less clear, as we show here. Figure 1 shows the EXAFS $k^2\chi(k)$ and $|\chi(R)|$ for room temperature Cu data, with the $R$-space plot shown out to $R = 31.4$ Å and on a log scale. For comparison, typical noisy spectra – one scan from a 2mM aqueous Zn(NO₃)₂ solution – is shown along with the Cu foil data. The noise levels estimated from the high-$R$ components of $\chi(k)$ are $\epsilon_k = 1.6 \times 10^{-4}$ for the Cu foil data, and $4.6 \times 10^{-4}$ for the Zn solution data. As can be seen from the log-scale plot of $|\chi(R)|$, the use of $R = [15, 25]$ Å to measure of the white noise in the Zn spectra is reasonable. On the other hand, the decaying $|\chi(R)|$ past 15 Å for the Cu data, and a comparison to the noise level in the Zn spectra suggests that the estimated $\epsilon_k$ for the Cu data may be too high. Of course, a smaller $\epsilon_k$ would increase $\chi^2_{\nu}$, not lower it. From this, we conclude that the estimate of $\epsilon$ cannot be off by enough to account for the large mis-fit. While such ideas as “systematic errors” and errors in background...
Table 2. Parameters for fits to room temperature Cu foil using FEFF6.0 and FEFF85 with MPSE. Fit ranges were \( k = [2, 16] \) Å\(^{-1}\), \( R = [1.65, 2.6] \) Å, with the Fourier transform using \( k \)-weight=2. A simple model for the 2nd shell and 1st-triangle paths was included to account for spectral leakage. For all fits, the parameters \( R \), \( \sigma^2 \), and \( E_0 \) were varied, and \( N \) fixed at 12. For the fit with FEFF6.0 and the first fit with FEFF85, \( E_i \) was set to 0 and \( S_0^2 \) varied. For the second fit with FEFF85, \( S_0^2 \) was set to 1 and \( E_i \) was varied.

| Parameter          | FEFF6  | FEFF85 \( (S_0^2) \) | FEFF85 \( (E_i) \) |
|--------------------|--------|----------------------|---------------------|
| \( R (\text{Å}) \) | 2.543(0.003) | 2.537(0.002) | 2.537(0.002) |
| \( \sigma^2 (\text{Å}^2) \) | 8.5(0.4) \times 10^{-3} | 7.8(0.3) \times 10^{-3} | 8.2(0.2) \times 10^{-3} |
| \( \Delta E_0 (\text{eV}) \) | 4.1(0.5) | 0.6(0.4) | 0.6(0.3) |
| \( S_0^2 \)     | 0.96(0.04) | 0.86(0.03) | 1.0 |
| \( E_i (\text{eV}) \) | 0.0 | 0.0 | 1.1(0.2) |
| \( \chi^2 \)   | 1012. | 584. | 360. |
| \( \chi^2 / \nu \) | 242. | 140. | 86. |
| \( R \)        | \( 1.6 \times 10^{-3} \) | \( 0.9 \times 10^{-3} \) | \( 0.6 \times 10^{-3} \) |

subtraction are often suggested as causes of the large mis-fits, we find these ideas difficult to quantify reliably. For data that is good enough to quantitatively analyze, we see no general evidence that \( \epsilon \) should be considered as anything but “white noise”. Instead, we suspect that the calculations themselves, while good enough to analyze the strongest peaks in the spectra, are far worse than the measurement uncertainties in these data.

3. Using FEFF8.5 with MPSE to model EXAFS

While the standard Hedin-Lundqvist exchange model[10] uses a single plasmon to account for the \( e^- - e^- \) contributions to the complex self-energy, the many-pole self-energy (MPSE) of Kas et al [7] replaces the one-particle plasmon pole with several plasmons with varying strengths chosen to match first-principle calculations of the low-energy limit of the inverse dielectric function \( \text{Im}[\epsilon(\omega)^{-1}] \)[11, 12]. While not easily calculated for all situations, these functions can be calculated for simple systems such as Cu metal. For the calculations used here, 10 poles were used to match to the dielectric function for Cu.

To test these many-pole self-energy calculations, we followed the same fit procedure described above for the same room temperature Cu K-edge data described above. A comparison of these fit results with those using FEFF6 are shown in Table 2. As can be seen, using FEFF85 and the MPSE improves the quality of the fit by about a factor of 2 compared FEFF6 using the standard 1-pole Hedin-Lundqvist exchange model we note that earlier versions of FEFF8 were no better than this FEFF6 calculation for this data on Cu metal. To test whether the remaining mis-fit was due to an incomplete accounting of the experimental energy broadening, we also performed a fit with \( S_0^2 \) fixed at 1 and \( E_i \), the imaginary part of the energy which broadens the spectra by altering the mean-free-path \( \lambda \), was varied instead. This model further improved the quality of the fit, finding that an additional 1 eV broadening lowered the value of \( \chi^2 / \nu \) to nearly 1/3 of that found with FEFF6. Because \( S_0^2 \) and \( E_i \) are very highly correlated, allowing them both to vary in the fit did little other than increase the error bars in all the parameters. Figure 2 shows the real components of the data and best fit model, varying \( E_i \) and fixing \( S_0^2 = 1 \) along with the fit residual. The oscillations in the residual are intriguing, and suggest that the remaining mis-fit should be explored further.
4. Conclusion
We have shown that the large absolute mis-fits in EXAFS analysis of high quality data using theoretical standards such as from FEFF are due primarily to errors in the calculations. As the biggest remaining approximation in these calculations is the inelastic losses (both intrinsic and extrinsic), we have tested the latest many-pole self-energy (MPSE) model in FEFF85 by comparing it with the standard Hedin-Lundqvist exchange model. The use of MPSE can dramatically improve the absolute fit quality. Furthermore, the fit quality can be improved by varying $E_i$ instead of $S_{02}$. If the MPSE exchange model can be applied to more complex systems, it may allow an improvement in all EXAFS analysis using theoretical standards, thereby improving the general precision and accuracy of the technique.

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