THE DIFFICULT CHORE OF MEASURING COORDINATION NUMBER WITH EXAFS

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Abstract
Neither the theory nor the interpretation of Extended X-Ray-Absorption Fine Structure (EXAFS) spectroscopy requires assumptions of crystalline symmetry or periodicity. As a result, EXAFS is a tool applied to a wide range of scientific disciplines and applied to a wide variety of experimental systems. One common use of the EXAFS measurement is the determination of coordination chemistry. A simple enumeration of the atoms in the coordination environment of the absorber is often the primary goal of an EXAFS experiment. There are, however, a number of pitfalls in the way of an accurate determination of coordination number. These include statistical limitations of the EXAFS fitting problem, empirical effects due to sample preparation or detector response, and the assumptions made about the physical structure surrounding the absorber in the course of data analysis. In this poster we examine several of these pitfalls and their effects upon the determination of coordination number. Where possible, we offer suggestions for avoiding or mitigating the pitfalls. We hope this poster will help guide the general EXAFS practitioner through the difficult chore of accurately determining coordination number.

Our favorite solution is to use your knowledge of your system to express the partial pair radial distribution function in a manner that actually represents the local structure. Here are some examples.

LOCAL DISORDER IN BARIUM TANTALUM OXYNITRIDE

Data were measured on the Ta K-edge of BaTaO2N at 10, 100, 200, and 300 K. Fitting the nominally cubic perovskite BaTaO2N using a cumulant distribution was unsuccessful. The fit quality was quite poor and the refined values of the fitting parameters were impossible to interpret as physically meaningful parameters. Subsequently, a structural model based on an energy minimization of a box of 4x4x4 unit cells. The different ionic sizes and electronegativities of O and N resulted in a multi-modal distortion to the local structure. The two- and three-body atomic arrangements from the energy-minimized box were collected in bins, as shown in the figures below. A FEFF calculation was made for each bin and the position and height of each bin was used as ∆R and ∆R in the EXAFS equation. Our fitting results suggest that this is a much closer representation of the structure. Although not perfect, the fit is vastly improved and the fitting parameters (including several σ^2 parameters and a lattice expansion coefficient) were all physically reasonable.

Fits to the BaTaO$_g$N Ta K-edge data measured at 100 K data using the cumulant and histogram models.

A Gaussian distribution may not be physically reasonable. Solvated metals, for example, have been successfully modeled using a Gamma distribution. The figure below shows the shape of the Gamma distribution superposed over a skewed Gaussian (i.e. with a third cumulant) using the same centroid, width, and skewness parameters.

The Gamma function drops sharply at low R and more gradually at high R. It's peak is also shifted inward from the same centroid. Using the skewed Gaussian in a situation where the Gamma should be used will introduce systematic error into your determination of coordination.

$$R_0 = 2.0 \text{ Å}$$
$$\sigma^2 = 0.003 \text{ Å}^2$$
$$C_3 = 0.0001 \text{ Å}^3$$

Skewed Gaussian and Gamma distributions using the same parameters and normalized to unit height.

S_0^2 AND COORDINATION NUMBER ARE COMPLETELY CORRELATED!

$$\chi_\Gamma(k) = \frac{N_\Gamma S_0^2 F_\Gamma(k)}{2kR_\Gamma^2} e^{-2k^2\sigma_\Gamma} e^{-2R_\Gamma/\lambda(k)} \times$$
$$\sin\left(2kR_\Gamma + \Phi_\Gamma(k) - 4k^3 C_{3,\Gamma}/3\right)$$
$$\chi_{total} = \sum_\Gamma \chi_\Gamma(k)$$

A simple fit to the first shell in aqueous gold hydroxide. The fit yielded an Au-O distance of 1.960(25) Å with σ^2 = 0.0029(11) Å. The insets show the raw data and the background-subtracted $\chi(k)$.

These data are the Au L_{III} edge of a gold hydroxide solution. The Au atom is coordinated by a hydration shell. A simple fit to a Gaussian distribution used parameters for ∆R, σ^2, Eo, and an **amplitude**. The refined value of the amplitude was 3.58 ± 0.40.

So what is the coordination number?

To extract a value for coordination from that measurement, we need a value for S_0^2. A fit to a gold foil gave a value of S_0^2 of 0.89 ± 0.06 by asserting the known coordination of the FCC structure. Using this and propagating uncertainty gives a coordination of 4.02 ± 0.52.

Another reasonable approach is to use FEFF8 or some other theory code to compute S_0^2 from first principles.

In any case, you must believe that the Gaussian distribution (or a cumulant distribution with C_3 and/or C_4) is an acceptable description of the distribution.

MODELING COMPLICATED DISTRIBUTIONS IN IFEFFIT

How could I use the Gamma distribution for gold hydroxide with Ifeffit?

$$f(r) = N \frac{p^{1/2}}{\sigma\Gamma(p)}\left[p + \left(\frac{r-R}{\sigma}\right)p^{1/2}\right]^{p-1} \times \exp\left[-p - \left(\frac{r-R}{\sigma}\right)p^{1/2}\right]$$

```
## Ifeffit script for a histogram representation of
## the Gamma-like distribution:

guess c3     = 0.0001
guess sigsqr = 0.003
guess rnot   = 2.0
guess enot   = 0
guess cn     = 6

def sigma    = sqrt(sigsqr)
def beta     = c3/sigma^3
def p        = 4/beta^2
def prefactor = cn * sqrt(p)/(sigma*gamma(p))

## bin at 1.850
def term01   = p + sqrt(p) * (1.850 - rnot) / sigma
path(1, file=feffNNNN.dat,
     n = 1, sigma2 = 0, third = 0,
     s02 = prefactor * (term01)**(p-1) * exp(-term01),
     e0 = enot)

## bin at 1.875
def term02   = sqrt(p) * (1.875 - rnot) / sigma
path(2, file=feffNNNN.dat,
     n = 1, sigma2 = 0, third = 0,
     s02 = prefactor * (term02)**(p-1) * exp(-term02),
     e0 = enot)

## bin at 1.900
def term03   = sqrt(p) * (1.900 - rnot) / sigma
path(3, file=feffNNNN.dat,
     n = 1, sigma2 = 0, third = 0,
     s02 = prefactor * (term03)**(p-1) * exp(-term03),
     e0 = enot)

## and so on ...
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AQUEOUS ZINC ON A RUTILE SURFACE

Aqueous Zn is typically coordinated by 6 O atoms but crystalline Zn may be coordinated by 4 O atoms. Zn adsorbed onto the rutile surface is may be 4- or 6-fold coordinated. Polarization-dependent EXAFS data was collected at the Zn K-edge. Using a simple, Gaussian oxygen shell to describe the polarization data, a seemingly reasonable fit is obtained. However, the amplitude of the O shell ranges from 5.6 to 10.4 with a very large σ^2 value of 0.020 Å^2, while a σ^2 value of 0.002 Å^2 is more typical for a Zn-O bond.

Density functional theory calculations found several possible sites for Zn on the rutile surface. These computed structures were used as models for the measured EXAFS spectra. In combination with XSW measurements, it was determined that there are three different coordination environments for Zn in this system including aqueous Zn above the rutile surface, a 4-fold Zn (R3) and a 4 to 6-fold Zn (R9). This final model fits the oxygen shell of all three polarizations as well as the Gaussian model, but also fits higher shells and yields physically sensible results.

R9 site: 4 to 6-fold coordinated

Approximate Amplitude of Path (%)			CN	R
Into	Par	Per		
100	100	100	1	1.84	Oa-Zn1
38	100	100	1	1.92	Od-Zn1
100	100	1	1.94	Oc-Zn1
100	23	2	2.69	Ob-Zn1
35	2	2.75	Of-Zn1
89	12	1	2.75	Oe-Zn1
35	14	1	3.11	Ti1-Zn1
24	20	1	3.33	Ti4-Zn1
14	55	1	3.52	Ti4-Zn1
11	34	1	3.52	Ti3-Zn1
11	32	1	3.88	Ti3-Zn1

R3 site: 4-fold coordinated

Approximate amplitude of path (%)			CN	R (Å)	Path
Into	Par	Per			
100	10	1	1.88	Oa-Zn1
100	85	1	1.94	Ob-Zn1
100	53	1	1.98	Oc-Zn1
100	15	1	2.05	Od-Zn1
23	1	3.31	O1-Zn1
25	1	3.37	O2-Zn1
23	1	3.47	O3-Zn1
20	1	3.49	Ti1-Zn1
23	1	3.58	Ti3-Zn1

6-fold aqueous Zn w/Zn-O bond length of 2.1 Å

Data	CN*S_0^2	R (Å)	σ^2 (10^3·Å^2)	∆E (eV)
		Zn-O		
Parallel	9 ± 4	1.98 ± 0.05	22 ± 11	-1 ± 4
Perpendicular	8 ± 1	2.02 ± 0.02	20 ± 4	2 ± 1
Into	8 ± 1	2.03 ± 0.02	19 ± 4	2 ± 2
4-fold Ref	4	1.96	-	-
6-fold Ref	6	2.10	-	-

Data	Percent	CN	R (Å)	σ^2 (10^3·Å^2)
Aqueous	39 ± 10 %	6	2.10	2
R9	20 ± 11 %	6	1.8 – 2.8	2
R3	41 ± 12 %	4	1.9 – 2.1	2
4-fold Ref		4	1.96	-
6-fold Ref		6	2.10	-

	Site R3			Site R9			
	x (Å)	y (Å)	z (Å)	Occu (%)	x (Å)	y (Å)	z (Å)	Occu (%)
DFT	0.44	0.55	3.18		1.64	1.37	2.40	
XSW	0.74(6)	0.31(12)	3.23(6)	59(10)	2.64(21)	1.48(47)	2.53(12)	20(6)
EXAFS	0.33(7)	0.43(9)	3.16(9)	41(12)	1.38(21)	0.71(21)	2.5(22)	20(11)

NORMALIZATION

Data are normalized to a unit edge step by regressing a line to the pre-edge region and quadratic to the post-edge region. The edge step is then the difference between the two polynomials extrapolated to the edge energy. The top spectrum shows the post-edge regression using Athena's default values for the range of the regression. The bottom shows a range chosen such the normalized white line was the same height as a standard believed to be the same material. These two choices result in different normalizations of $\chi(k)$. This effect is correlated to the determination of correlation in the exact same manner as S_0^2.

Care must *always* be taken when processing data. A good determination of coordination number begins at the very first step!

These quantities are highly (or completely) correlated with one another:
1. coordination number
2. S_0^2
3. $F_{t_0}(k)$
4. σ^2
5. normalization
6. empirical effects, such as a self-absorption, detector non-linearity, or sample inhomogeneity

Effect of normalization parameters on the evaluation of the edge step normalization for a U^{6+} compound. The circles show the range over which the post-edge regressions were performed.

Conclusion
Accurate determination of coordination number is not trivial in EXAFS data analysis. At best, coordination number must be interpreted from the amplitude term refined in a fit, given that coordination is highly or completely correlated to S_0^2 and to various aspects of sample preparation and data processing.

For complicated systems, accurate determination of coordination number requires sophisticated structural modeling. Any information that can be drawn form other measurements or from theory of some sort can be leveraged to solving the EXAFS problem. The references box cites several examples of using a path expansion for complicated, non-Gaussian distributions. A variety of useful tutorials and presentations discussing the many issues covered in this short paper can be found on the web at http://xafs.org.

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