SESAME

Synchrotron-light for Experimental Science and Applications in the Middle East

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EXAFS data fitting

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Acknowledgment

Some slides are copied from other presentations by

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Goals

- Main goal is to learn the basics of how to perform shell fitting of EXAFS data using Artemis (*if time allows we can try WinXAS also*)

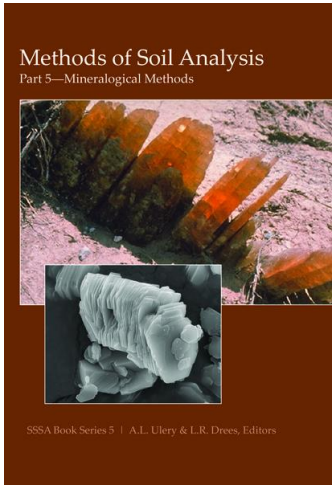
- Present basic techniques to fit "shells" of a Fourier transformed EXAFS spectrum
  - Briefly illustrate background subtraction & normalization
  - Provide a basic "protocol" for getting data loaded and starting a fit

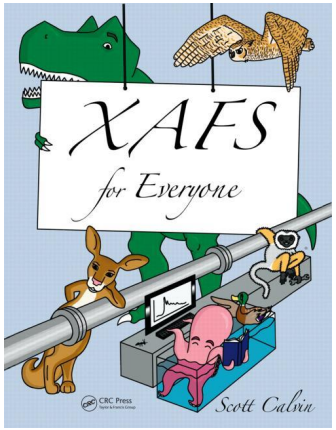
- A "short course" to give you the skills to learn how to fit and provide learning resources
  - Cannot be learned in one day, or few days
  - Each system is distinct (crystalline, amorphous, sorption …)

Resources

- Software help with Demeter (Athena, Artemis)
  - http://bruceravel.github.io/demeter
- Video tutorials on Artemis
  - https://vimeo.com/channels/exafs
- IFEFFIT Mailing list
  - https://www.mail-archive.com/ifeffit@millenia.cars.aps.anl.gov
- *Shelly Kelly et al., 2008. Soil Science Society of America, Methods of Soil Analysis. Part 5. Mineralogical Methods. Analysis of Soils and Minerals Using X-ray Absorption Spectroscopy, Chapter 14
- *XAFS for Everyone (2013) by Scott Calvin
- **Many more resources listed at end of presentation**

https://matthewsiebecker.com/xas-videos/





*many figures in this presentation are copied straight from these resources

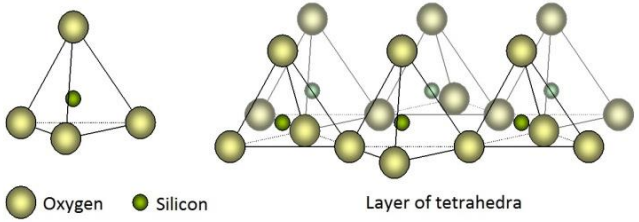
Purpose of EXAFS Shell Fitting

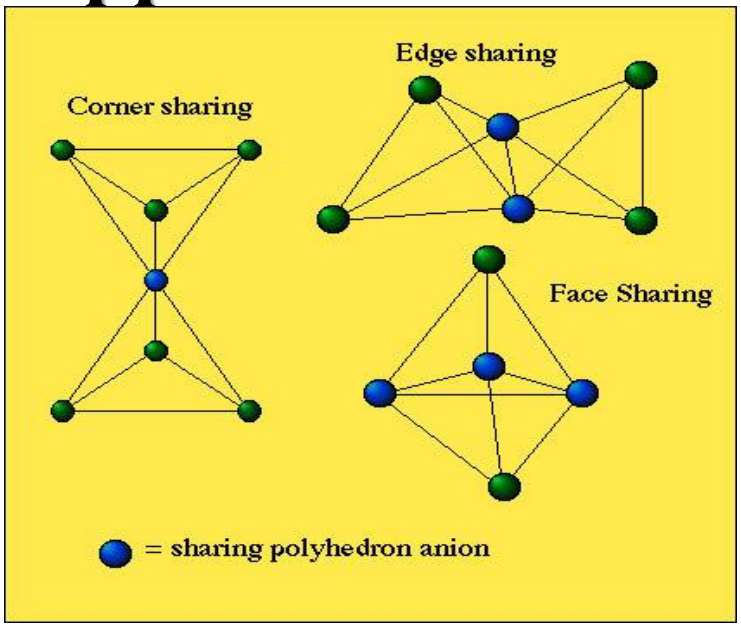
- What is the purpose of EXAFS shell fitting?
  - determine inter atomic distances (distances between neighboring atoms)
  - determine coordination number (number of atoms at a specific distance)

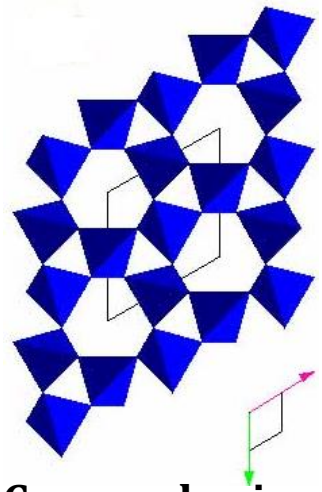
- What can we do with this information?
  - confirm or disprove our hypotheses about the chemical species in which we are interested

- Generally the polyhedral approach is employed to understanding sorption, desorption, molecular bonding on mineral surfaces, atomic substitutions and defects in the structure, ….

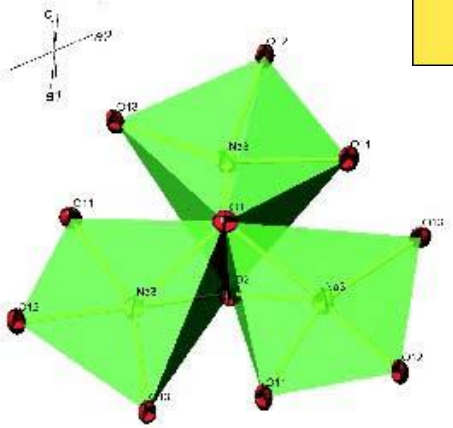
The Polyhedral Approach



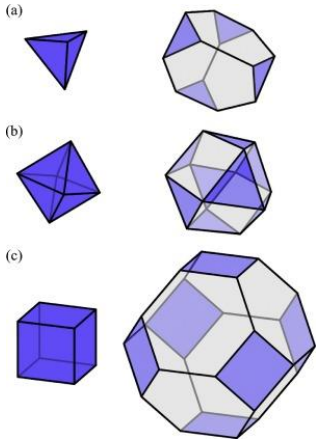




Corner sharing

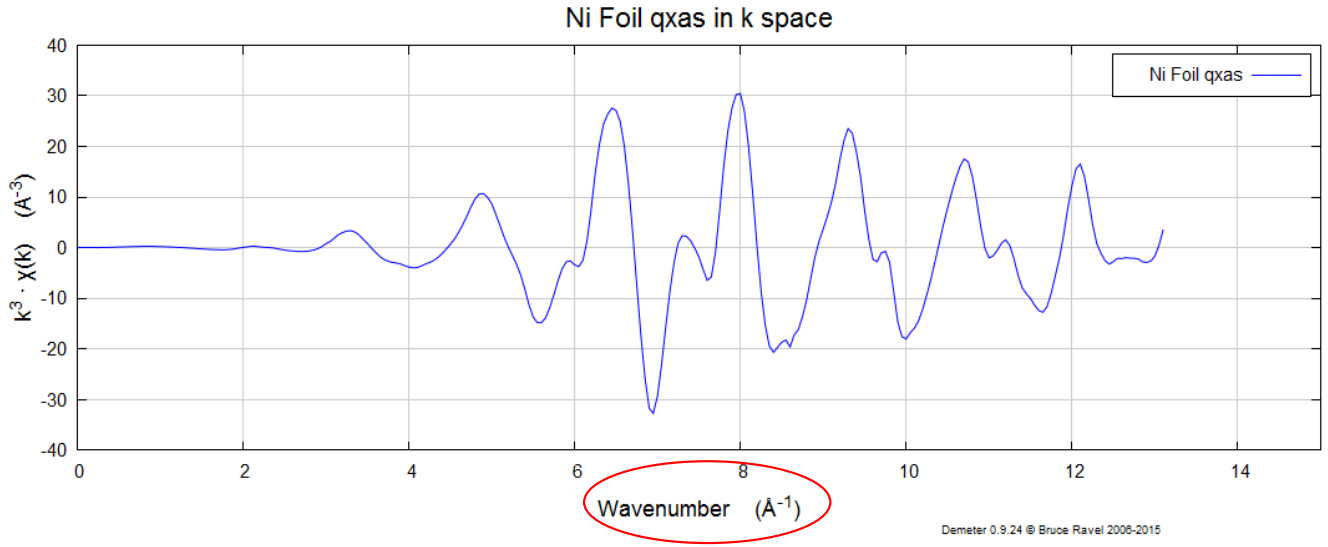


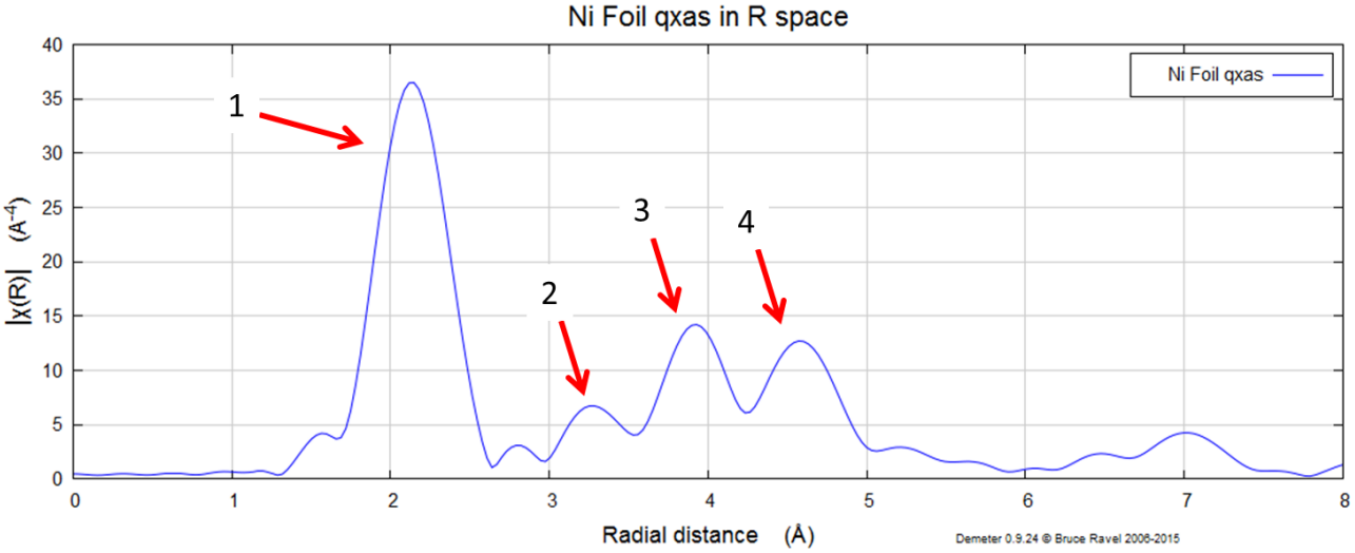
Edge sharing



surface sharing

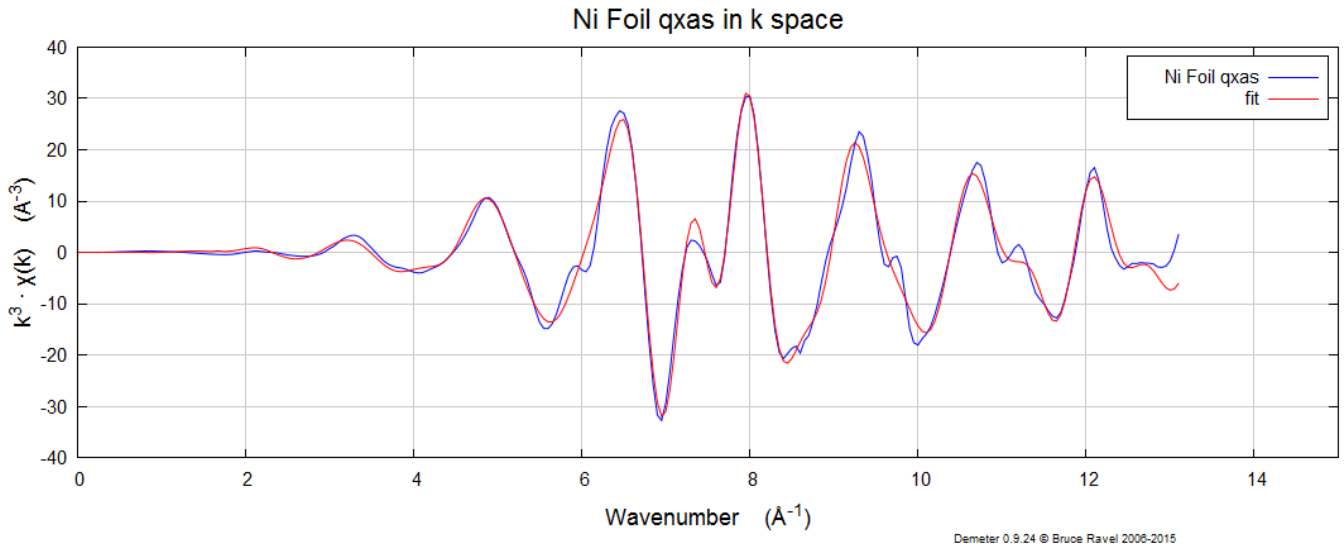
What is a “shell” ?





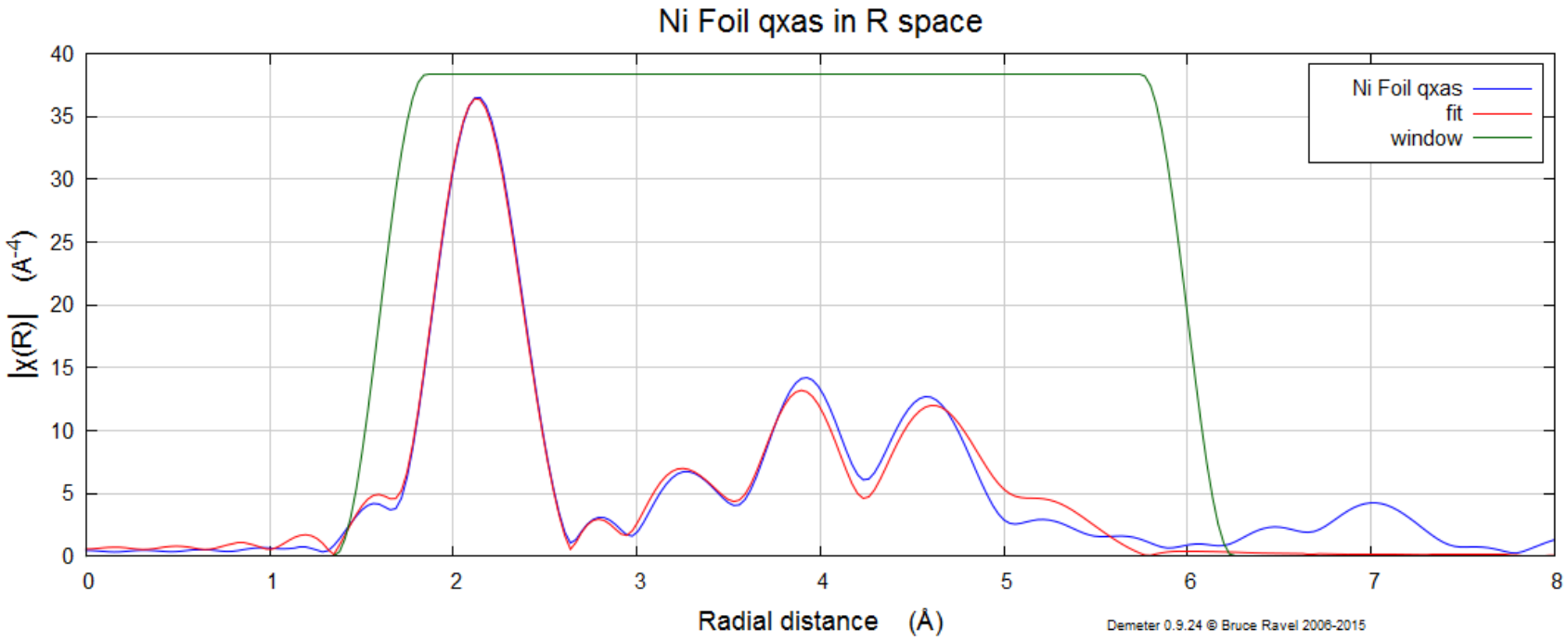
How do we do EXAFS shell fitting?

- ❑ Try to get the squiggly lines to lie on top of each other
- ❑ Get the red line [the fit] follow the blue line [the data]
- ❑ Create a model that "fits" the data



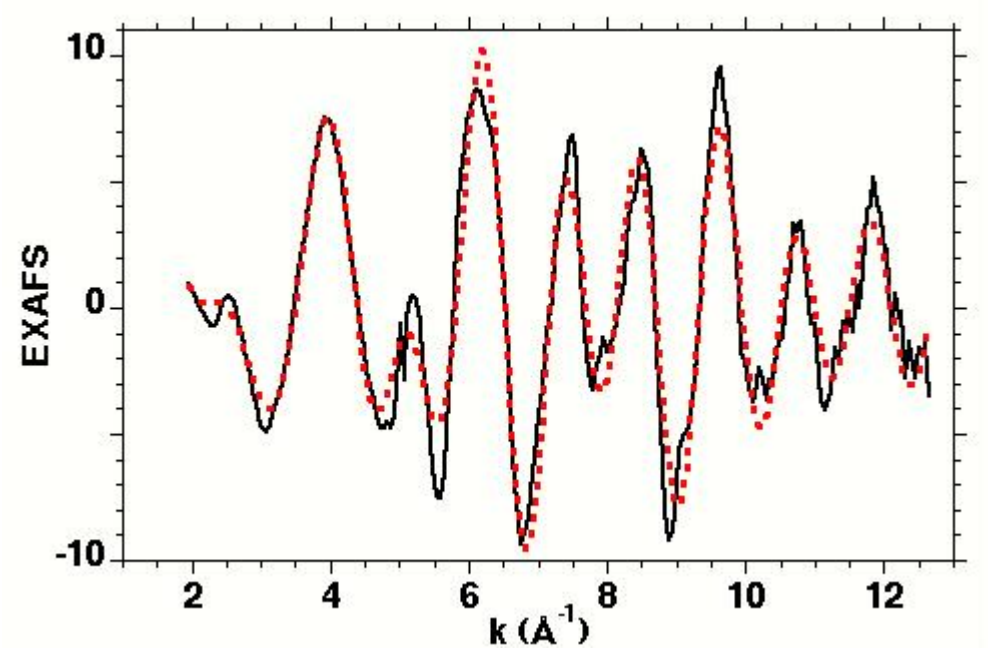
EXAFS shell fitting

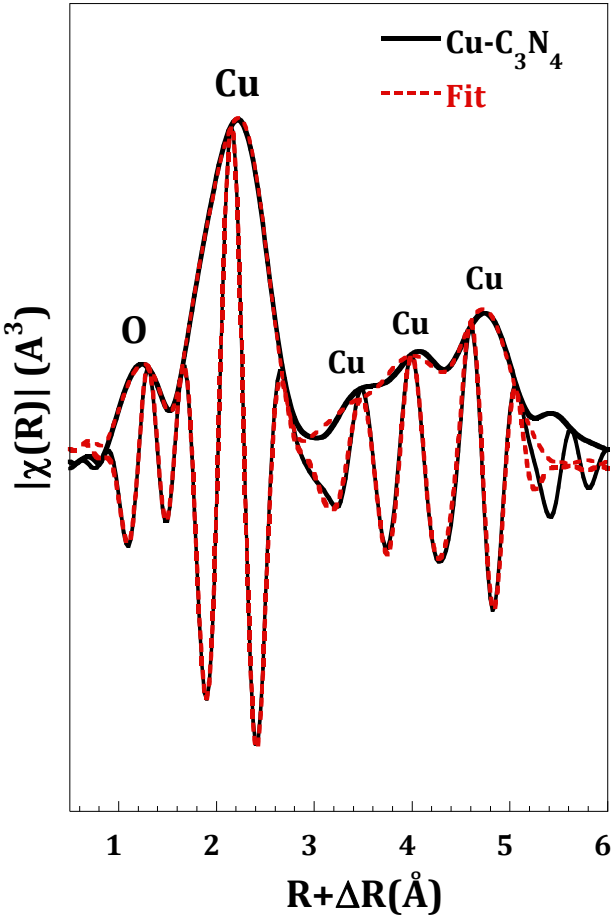
A graphically (visually) "good" fit is not definitive. The statistical results and calculated values tell the real story of the fit (quantitative results).



EXAFS shell fitting

- **EXAFS are modelled to derive structural parameters**





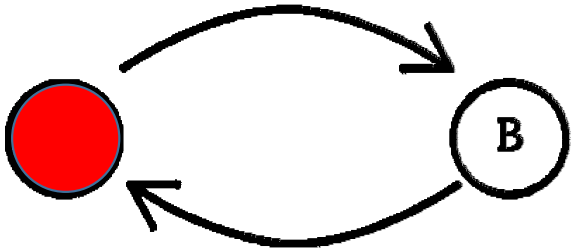
What statistical results and calculated values?

- There are in general five (5) variables that you fit. These variables are part of the EXAFS equation.

- The EXAFS equation describes the features seen in EXAFS data (e.g., amplitude and frequency of oscillations)
  - to determine interatomic distances and coordination number we fit five variables that are part of the EXAFS equation.

- Create the best fit possible with the least number of fitted variables
  - "BEST FIT" = physically realistic values with lowest amount of misfit using least amount of fitted variables
  - R-factor, "chi square" (χ^2), "reduced chi square" (χ^2_v)
  - Using constraints based on prior knowledge about the sample
    - Crystal structure, predicted interatomic distances, disorder (amorphous vs, crystalline)

How do we fit?



A single scattering path (back and forth)

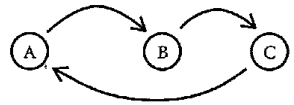


Figure 14.5 A focused path.

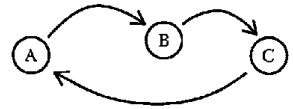


Figure 14.6 A partially focused path.

Figure 14.7 A double path.

We "fit" scattering paths of the photoelectrons.
Those paths are based of off models.

Funke et al 2007, doi:10.1107/S0909049507031901

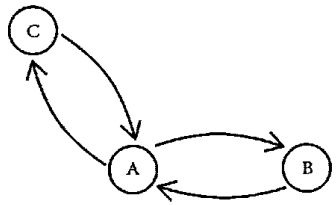


Figure 14.8 A conjoined path.

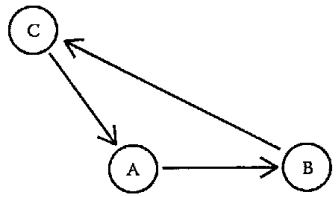


Figure 14.9 A triangle path.

Calvin, 2013

What do we fit?

- There are in general five (5) variables that you fit. These variables are part of the EXAFS equation.

The EXAFS spectrum can be understood in terms of the EXAFS equation. The EXAFS equation can be written in terms of a sum of the contribution from all scattering paths of the photoelectron (Stern, 1978; Stern and Heald, 1983):

$$\chi(k) = \sum_i \chi_i(k)$$

Each path can be written in the form:

$$\chi_i(k) \equiv \frac{\left(N_i S_0^2\right) F_{\mathrm{eff}_i}(k)}{kR_i^2} \sin\left[2kR_i + \varphi_i(k)\right] e^{-2\sigma_i^2 k^2} e^{\frac{-2R_i}{\lambda(k)}}$$

1 , 2

3

with 5

$$R_i = R_{0i} + \Delta R_i$$

and 4

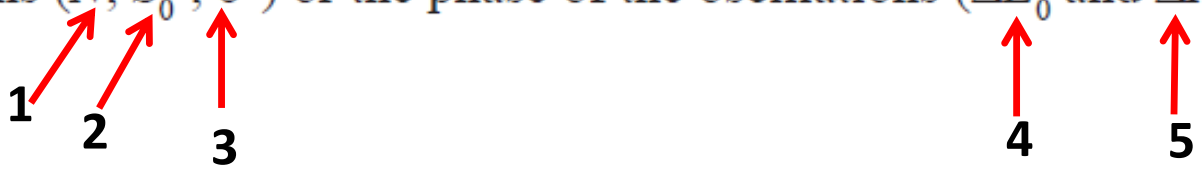
$$k^2 = \frac{2m_e\left(E - E_0 + \Delta E_0\right)}{\hbar}$$

- To know specifically what each variable stand for in the EXAFS equation, see previous presentation (see also Shelly 2008.
- Many of the terms can be calculated by a computer program such as FEFF, we are only going to focus on the five generally concern us as users

What do we fit?

$$\chi_i(k) \equiv \frac{\left(N_i S_0^2\right) F_{\text{eff}_i}(k)}{kR_i^2} \sin\left[2kR_i + \varphi_i(k)\right] e^{-2\sigma_i^2 k^2} e^{\frac{-2R_i}{\lambda(k)}}$$

Once a path has been selected for possible inclusion in a structural model, mathematical expressions for the EXAFS parameters (Eq. [5]) are defined. The parameters that are often determined from a fit to the EXAFS spectrum affect either the amplitude of the EXAFS oscillations (N, S_0^2, σ^2) or the phase of the oscillations (ΔE_0 and ΔR).



(1) N – coordination number (CN),
(2) S_0^2 – Amplitude reduction factor
(3) σ^2 – the disorder term
(4) ΔE – the change in energy from theoretical data
(5) ΔR – the change in interatomic distance

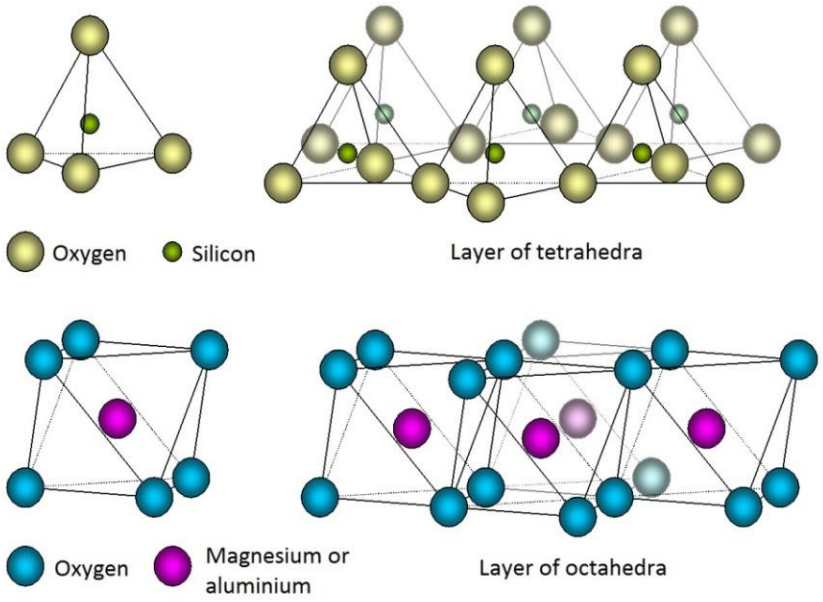
Fitting variable "N"

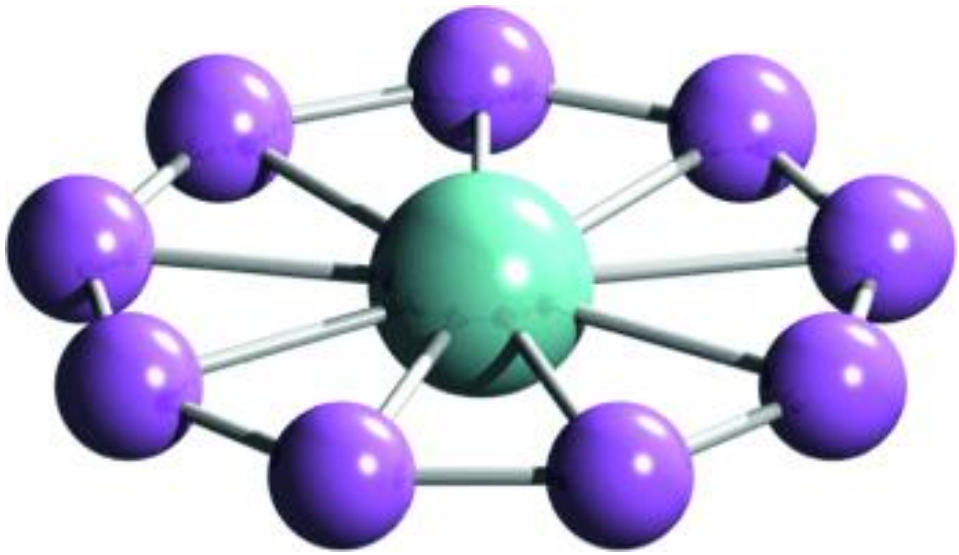
N - coordination number (CN)

- Degeneracy (the number of equal path lengths)
- Typical values – never negative, generally less than 8 for oxides for single scattering
- When fitting a "standard" this value can be constrained to equal the CN of the model to determine S_o^2
- Generally for the first shell, we have an idea about its value
  - For the next shells, It is guessed when fitting an unknown CN (e.g., sorption sample or precipitate)

Fitting variable "N"

N - coordination number (CN)





Fitting variable "S_0^2"

S_0^2 - Amplitude reduction factor

- Accounts for the slight relaxation of the remaining electrons in the presence of the core hole vacated by the photoelectron
- Is different for different elements, but the value is generally transferable between different species from the same element and the same edge (chemically transferable)
- Acceptable values
  - Should be "a bit less than 1"
  - 0.7 to 1.05 are reasonable, normal values commonly seen between 0.8 an 1
- Constraint: it should be the **same** value for every scattering path (all paths use the same value)
- Can be determined from the fit of a "standard" (e.g., well defined mineral or aqueous ion)
- Can be fixed to 0.9 but you ***must*** account for the added uncertainty to the CN (see how to do this in Calvin, 2013)
- Directly correlated to CN!

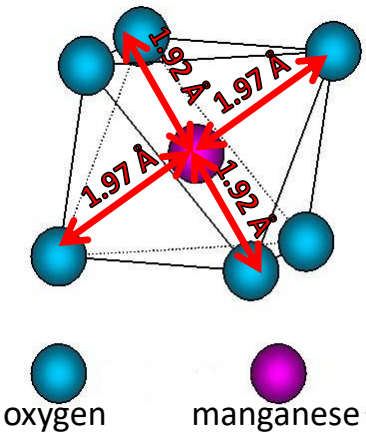
$$\chi_i(k) \equiv \frac{\left(N_i S_0^2\right) F_{\mathrm{eff}_i}(k)}{kR_i^2} \sin\left[2kR_i + \varphi_i(k)\right] e^{-2\sigma_i^2 k^2} e^{\frac{-2R_i}{\lambda(k)}}$$

Fitting variable "σ^2"

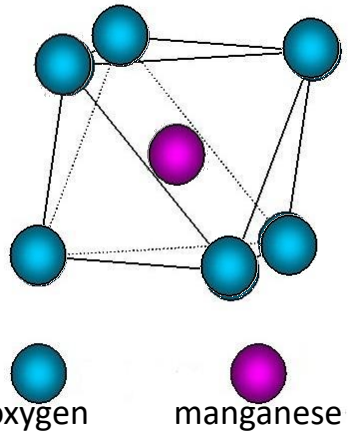
σ^2 - Sigma squared, MSRD

- The Mean Square Relative Displacement (MSRD)
  - Debye-Waller factor
- It is the variance in the half path length
  - the square of the standard deviation of the half path length
- Describes static and/or thermal disorder term

STATIC DISORDER



THERMAL DISORDER



Fitting variable "σ^2"

σ^2 - Sigma squared, MSRD

- In general, the values for σ^2 become bigger with increasing bond length or shell number (*Kelly et al., 2008*)
  - E.g., 0.006 for first shell, 0.01 for second shell
- Typical values: 0.002 to 0.03 Å^2, if any larger, the path is so disordered that it is contributing little to the fit which can be a sign the model is wrong in some way (Calvin, 2013)
- There are many, many ways to constrain this variable:
  - Use one value "constrain" for atoms of similar type (Z) and similar distance
  - Constrain values for atoms overlapping in their error bars
  - Use one value for the first shell and one value for the second shell
  - See Calvin, 2013 for more discussion

Fitting variable "ΔE"

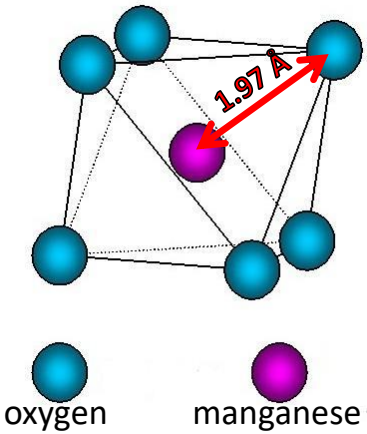
ΔE – "delta E"

- This term relates to a change in the photoelectron energy and is used to align the energy scale of the theoretical spectrum to match the measured spectrum (Kelly et al., 2008)
  - https://www.researchgate.net/publication/237626147_EXAFS_Energy_Shift_and_Structural_Parameters
- In general, these shifts should be less than 2 to 3 eV
  - See "Aligning Energy Scales of Experimental and Theoretical Spectra" in Kelly et al., 2008 for adjust for shifts larger than this
  - Generally, for "decent data" and a good fit E_0 has uncertainty of 0.5 to 1.0 eV (IFEFFIT mail list)
- E_0 should always be on or near the rising portion of the edge, never on the smooth pre-edge or in the EXAFS region (Calvin, 2013)
- Constraint: Use one ΔE for all scattering paths

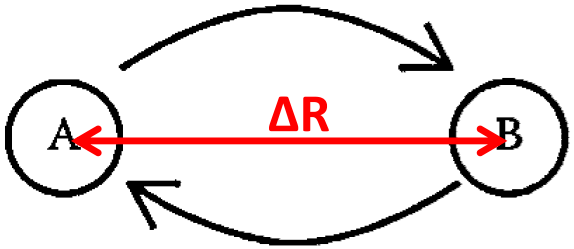
Fitting variable "ΔR"

ΔR – "delta R"

- This term represents a change to the interatomic distance relative to the initial path length
- Interatomic distance is the same thing as half path length, where path length is the length of the complete scattering path
- Constraints: isotropic *expansion–contraction* term applied to all paths (good for cubic systems) *or* values can be grouped depending on path length or direction (Kelly et al 2008)
- Generally, for "decent data" and a good fit, R has uncertainty of 0.01 or 0.02 Å (IFEFFIT mail list)

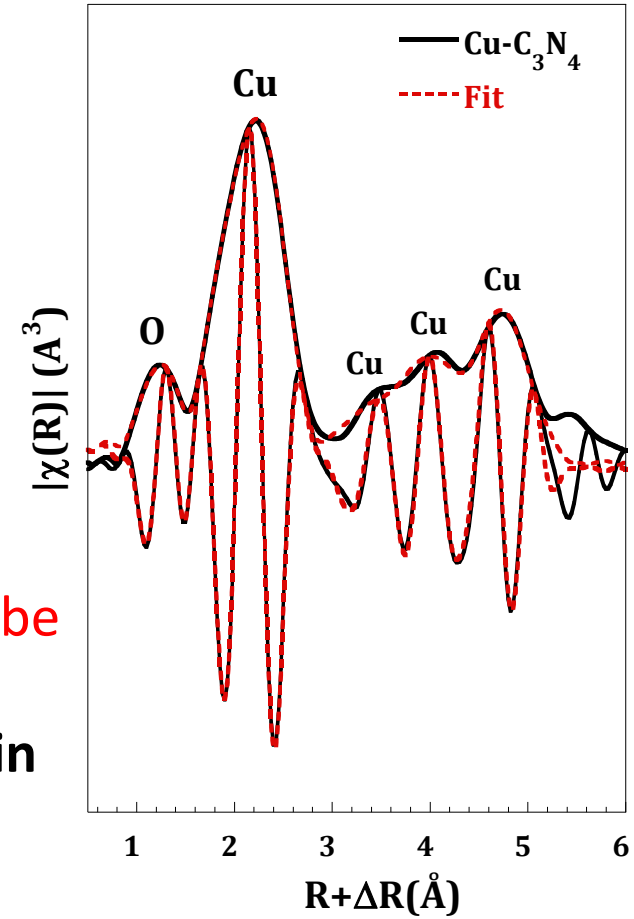


For example:
if R_i = 1.97
and R = 2.04
then **ΔR = 0.07**



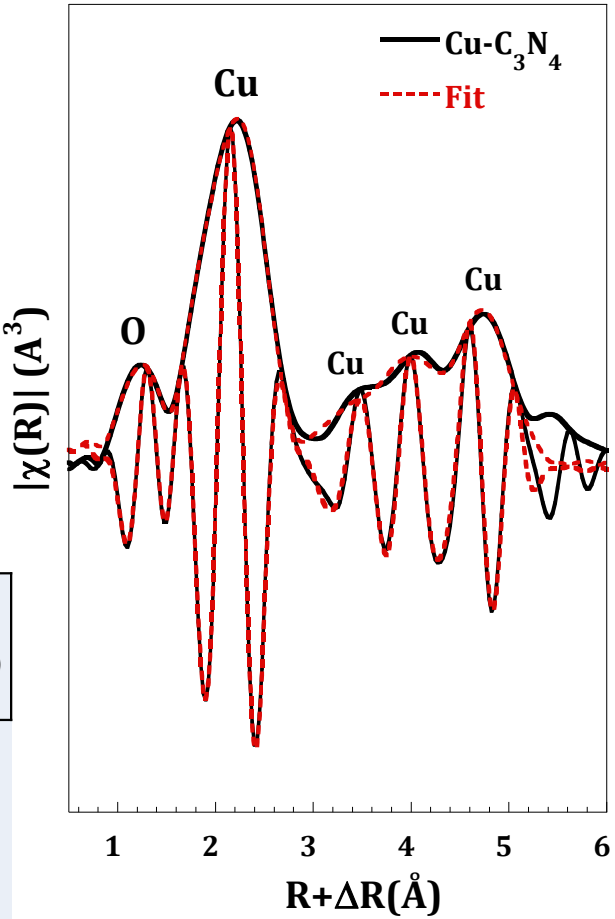
Fit statistics – Goodness of the fit

- Statistical parameters (the standard goodness-of fit parameters) include:
  - the number of independent points, N_{idp}
  - the number of variables, N_{var}
    - must be less than N_{idp}
  - "chi square" (χ^2)
  - "reduced chi square" (χ^2_v)
  - R-factor
  - All these values are calculated by the software (except N_{var})
- The isolated EXAFS signal is denoted as $\chi(k)$ and should not be confused with the goodness-of-fit parameter χ^2
- **The *R* factor is a major fit parameter that can be included in the published table**



What parameters to publish?

Bond	N (atom)	R (Å)	σ^2 (Å^2)	ΔE (eV)
Cu-O1	2.2(02)	1.785(2)	0.00332(5)	2.6(1)
Cu-O2	6.7(05)	1.934(3)	0.01109(3)	-8.6(1)
Cu-Cu1	3.4(07)	2.534(1)	0.01193(1)	4.6(2)
Cu-Cu2	7.1(1)	3.638(5)	0.01305(2)	8.9(8)
Cu-Cu3	5.4 (05)	4.337(4)	0.01332(8)	-3.4(4)
Cu-Cu4	6.6(03)	5.163(2)	0.017875(3)	-7.3(2)

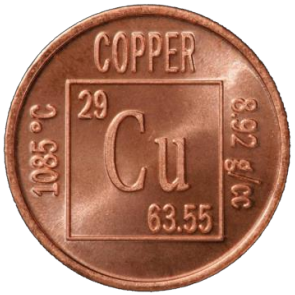


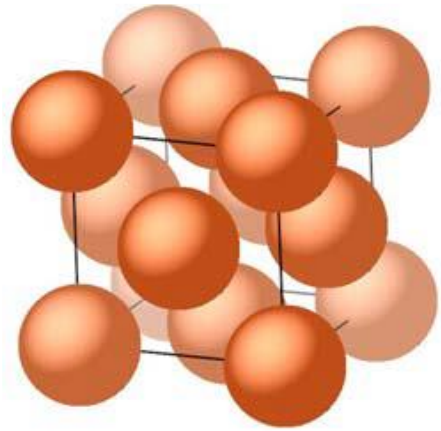
Sample & CIF reference	R-factor & # in Table 5	N_{idp} & k-range fit	N_{var} & R-range fit	χ^2 & χ^2_n	Path	CN	R (Å)	σ^2 (Å^2)	ΔE (eV)	±CN	±R (Å)	±σ^2(Å^2) x10^{-3}	±ΔE (eV)
Ni-Acid birn.	0.007	13.5	9	3674	Ni-O	6.4	2.055	0.006	0.9	1.1	0.010	2	1.0
(Post and Veblen, 1990)	8	2.5 - 11.5	1.2 - 3.6	823	Ni-Mn	1.2	2.886	0.008	0.9	0.5	0.030	3	1.0
					Ni-Mn	5.5	3.494	0.008	0.9	1.7	0.014	3	1.0

Let's Start Fitting – Cu foil

- Athena
  - Data normalization
  - Illustrate back FT in Athena
    - Expanding R- range changes the back-FT reproduce smaller feature from higher shells and MS paths

- Artemis
  - Shell Fitting
  - For a clear explanation of the windows and buttons used in Artemis, see videos by its author (Bruce Ravel):
    - https://vimeo.com/channels/exafs





by Latif Ullah Khan (beamline scientist of XAFS/XRF beamline at SESAME)