

(Temporary Title)

Investigation of Bond Strain Effects on XANES Spectra by Supervised Machine Learning

by
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Abstract

A recently published method [1] enables the decoding of X-ray absorption near edge structure (XANES) spectra of nanoparticles to obtain important structural descriptors: coordination numbers and bond distances. Utilizing supervised machine learning (ML), the method trains an artificial neural network (ANN) to recognize a relationship between the nanoparticle structure and the XANES spectrum. Once trained, the ANN is used to “invert” an unknown spectrum to obtain the corresponding descriptors of the catalyst structure. Bond strain is known to be an important catalytic descriptor, yet, its accurate determination in reaction conditions is hampered by high temperature and low weight loading of real catalysts. ML-assisted XANES analysis offers a promising new direction for extracting the bond strain information from XANES—and not from extended x-ray absorption fine structure (EXAFS) analysis. Using simulated XANES spectra of Au nanoparticles, we have developed an ANN capable of “inverting” an unseen XANES spectrum and predicting structural disorder in the form of mean-squared displacement. The utility of the method was demonstrated on both the computer-simulated nanoparticles of different sizes and degrees of disorder, as well as on experimental data of disordered nanoparticles.

Executive Summary

Your executive summary will give a detailed summary of your thesis, hitting the high points and perhaps including a figure or two. This should have all of the important take-home messages; though details will of course be left for the thesis itself, here you should give enough detail for a reader to have a good idea of the content of the full document. Importantly, this summary should be able to stand alone, separate from the rest of the document, so although you will be emphasizing the key results of your work, you will probably also want to include a sentence or two of introduction and context for the work you have done.

Acknowledgments

The acknowledgment section is optional, but most theses will include one. Feel free to thank anyone who contributed to your effort if the mood strikes you. Inside jokes and small pieces of humor are fairly common here . . .

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Chapter 1

Introduction

Synchrotron radiation was first observed by General Electric in Schenectady, New York [2]. Initially just a side effect of particle accelerator experiments, it has since grown to be an important and powerful source of high-energy electromagnetic radiation for structural determination. Compared to lab-scale x-ray generation for diffraction experiments, arguably the most important benefit of synchrotron radiation is its high brilliance. Synchrotron radiation creates a highly collimated beam of photons characterized by small divergence and spatial coherence. Additionally, synchrotron radiation is tunable across a wide spectrum (microwaves to hard X-rays) and capable of high flux, useful for short time-scale-dependent experiments or weak scatterers. Synchrotron radiation can be produced in a pulsed structure. Importantly, the incoming photons are highly polarized, either linearly or circularly, depending on where the measurement system lies with respect to the plane of the synchrotron. The advent of a technique to manufacture such a high-quality source of x-rays allowed for new, advanced methods of x-ray absorption spectroscopy, and the two fields were developed in parallel.

frequency
range?

1.1 X-ray Absorption Spectroscopy

X-ray absorption spectroscopy measures the absorption of high-energy photons by a sample as a function of energy [3]. The attenuation, or change in transmitted light intensity as a result of inelastic processes, is characterized by the Beer-Lambert Law (1.1). For an incident beam of intensity I_0 , the transmitted intensity after interacting with an attenuator/absorption coefficient of μ and a sample of thickness x is:

pick one

$$I = I_0 e^{-\mu x} \quad (1.1)$$

Above the absorption edge, the condensed state has characteristic absorption jumps where the incident photon's energy matches the binding energy of a core electron. At this energy, nearly all the photon's energy is absorbed by the core electron, resulting in the characteristic absorption-edges first observed in 1920 [4, 5].

In experimental setups, particular energy photons are selected from the broad spectrum of synchrotron radiation via a pair of monochromators. The primary monochromator is a

crystal with interplanar spacing, d , chosen specify to satisfy the Bragg equation 1.2, selecting photons of wavelength, λ at angle θ .

$$n\lambda = 2d \sin(\theta) \quad (1.2)$$

The secondary monochromater removes higher order harmonics that satisfy the Bragg equation ($2\lambda, 3\lambda$ etc.). Different wavelengths of light can be selected by changing the angle. In the XAFS setup, two ionization chambers are used to measure the incident and transmitted light intensity. For any study, the absorption spectrum for a reference sample is also measured to calibrate the energy scale.

1.1.1 XAFS

X-ray Absorption Fine-Structure (XAFS) spectroscopy refers to the study of absorption spectra created from high-intensity x-ray interactions. As the energy of the incident radiation increases, the photon's energy will eventually match the binding energy of a core-level electron. As a result, an "edge" in the spectrum will be observed. The location of these edges depends on the chemical and physical structure, as well as the electronic and vibrational states of the material. Absorption edges are like fingerprints used to identify elements, distinguish oxidation states, and even probe short-range order from the characteristic peaks and oscillations in the spectrum. XAFS spectroscopy can be performed on virtually any stable element since all atoms contain core-level electrons. Although a high-quality source of x-rays such as synchrotron radiation is required for the analysis, the ubiquity and utility of XAFS spectroscopy has made it an indispensable technique in fields such as materials biology, chemistry, and materials science [6] [7].

The XAFS equation is

$$\chi = \frac{\mu(E) - \mu_0(E)}{\mu_0(E) - \mu_b(E)} \quad (1.3)$$

where μ is the measured absorption, μ_0 is the "atomic" absorption due to specific electrons, and μ_b is the absorption of other processes [8], typically approximated with the Victoreen polynomial (1.4).

$$\mu_b(E) = aE^{-3} + bE^{-4} \quad (1.4)$$

The coefficients α and β can be found via a simple regression on a spectrum measured at pre-edge energies [8].

The XAFS spectrum is typically divided into two regions of study: the area near the first absorption peak —XANES, and the area after —EXAFS. XANES has a strong sensitivity to the oxidation state and coordination chemistry of the absorbing atom, while the EXAFS can be used to determine the bond lengths, coordination numbers, and atomic species of the absorbing atom's neighbors.

1.1.2 EXAFS

Beyond the edge of the absorption spectrum lies the Extended X-ray Absorption Fine Structure (EXAFS) region. The spectral shape of this domain is determined by the multiple scattering of the photoelectron, interference of the incoming and outgoing waves of the photon, and electronic energy level splitting of the local structure. The oscillations in the EXAFS region are extremely sensitive to local bond lengths, coordination numbers, and atomic species of the surrounding elements.

EXAFS Data Reduction

To prepare the absorption data for fitting (data reduction), several steps must be performed. First the pre-edge background must be removed using the Victoreen formula (1.4) or an alternative polynomial. Next, the atomic background, $\mu_0(E)$ is removed and the absorption measured absorption is normalized accordingly. This is a non-trivial process, as the absorption coefficient is not that of a single, isolated atomic absorber, but instead of an atom and its surrounding neighbors. High order spline fittings must be used to remove the low frequency, immeasurable oscillations due to photoelectron scattering with nearby valence electrons. For EXAFS Fitting, the EXAFS function is often transformed into k-space, and Fourier transformed into a radial distribution-like function via [9].

$$\tilde{\chi}(r) = \frac{1}{2\pi} \int_0^\infty k^n \chi(k) e^{2ikr} dk \quad (1.5)$$

Alternatively, one can convert the wave to R-space, which is what Artemis and Athena, two of the most common EXAFS fitting software, do.

The EXAFS Equation

With the data reduction complete, a multi-parameter fitting can be performed via the EXAFS equation. This equation is an approximation based principally on Fermi's golden rule (1.6).

$$\mu(E) \propto \sum_f^{E_f > E_F} |\langle f | H_{int} | i \rangle|^2 \delta(E - E_F - Ef) \quad (1.6)$$

At energies above the core electron binding energy, the excess energy is transferred to the photoelectron, which may then undergo multiple scattering with the surrounding atoms. The final wavefunction of the photoelectron is then the superposition of the outgoing photoelectron and the scattered

$$\chi(k) = \sum_j \frac{N_j}{kr_j^2} F_j(k) e^{-2\sigma_j^2 k^2} e^{-\frac{2r_j}{\lambda(k)}} \sin(2kr_j + \phi_{ij}(k)) \quad (1.7)$$

While popular, the EXAFS equation is still a first order approximation with its own assumptions and limitations. For example, the fitted disorder parameter, the Debeye-Waller factor, explicitly assumes a Gaussian distribution of nearest-neighbor bond length distances. Other, more accurate but computationally intensive alternatives, such as molecular dynamics, reverse monte carlo simulations, and neural networks are increasing in popularity.

1.1.3 XANES

While there is an “EXAFS Equation,” there is no “XANES Equation” equivalent. With the recent explosion in popularity of machine learning in science, a modern topic of research is to determining how much information is encoded in the XANES region.

1.2 Disorder in XAFS

1.3 Nanoparticles?

1.4 Machine Learning?

Probably want to talk about these papers in this section [10] [1].

1.5 Outline of the Thesis

Building off the historical context of measuring disordered nanoparticles in XANES spectra, this thesis begins with an in-depth description of

Chapter 2

Simulating Disorder

Before making any predictions, neural networks must first be trained on a large quantity of data. Specifically, to teach our neural network to predict the mean squared displacement (MSD), we must first generate a large quantity of training data comprised of XANES spectra, each labeled with a known MSD. Gathering such a large quantity of high-quality experimental data would be impractically time-intensive and expensive. Rather, simulations provide a practical alternative, though even simulating each possible disordered structure individually, would be extremely time-intensive. Instead, we run many XANES simulations of simple, non-disordered structures and generate the neural network training data or disordered spectra via clever statistical averaging. In this chapter, we explain this statistical weighting process in-depth, beginning with the creation of simple, non-disordered spectra for the FEFF input files and culminating in the creation of many possible disordered spectra with known MSD.

Of just Au NPs? Can we generalize this to the sigma of the PRDF?

Maybe give a brief outline of the process so you can understand the point of the sections as a walk-through before the very end

2.1 Generating Distortion Not Disorder

Instead of creating structures with a range of *disorder*, we instead begin by generating structures with a range of *distortion*. Whereas *disorder* refers to a statistical average of atomic displacement from their original position, characterized by MSD and the width σ^2 of a partial radial distribution function, *distortion* refers only to an isotropic expansion or contraction of the subject. Equivalently, we define distortion as a radial shift in all atomic positions away from (or towards) the center atomic absorber.

A 2-dimensional projection of this isotropic distortion is presented in Figure 2.1. Though the figure only shows the xy -plane projection of the first 12 nearest neighbors, the actual structure used consists of the first four shells (55 atoms) with a lattice constant of 4.0782 Å to match that of bulk Au. In reality, the nearest-neighbor distances for Au nanoparticles are likely smaller ; this can be accounted for later on in the averaging process since the original coordinates will only be one structure out of many. The important part is that the crystal

Citation? Wolfram Element Data?

citations?

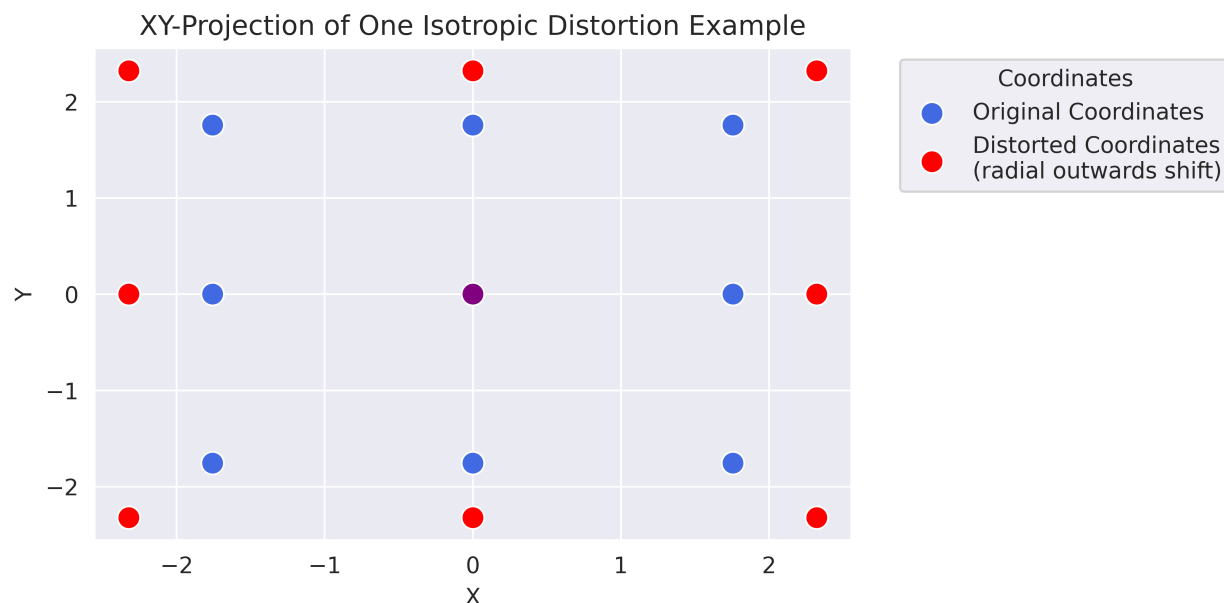


Figure 2.1: Each point represents an atom of first 12 nearest neighbors of a Au cluster projected onto the xy -plane. The four corner points actually represent two atoms because of the projection. The blue atoms represent the original coordinates, and the red atoms represent the radially shifted coordinates. The center absorber atom is purple since its original position is the same as its distorted position.

structure is correct.

We generate a total of 91 FEFF input files with different levels of distortion. Each file contains the same center absorber located at $(0, 0, 0)$, but all other atomic coordinates are in a shifted location on the range of -0.45 \AA to $+0.45 \text{ \AA}$ in increments of 0.01 \AA . For example, the FEFF input file with the greatest inward shift has all coordinates shifted 0.45 \AA radially inwards towards the center absorber, and the FEFF input file with the largest outwards shift has coordinates shifted 0.45 \AA radially outwards away from the center absorber.

Each FEFF input file is run with the following parameters:

```

1      SCF 4.6 0 30 .5 1
2      EDGE      L3
3      EXCHANGE      5      0.2 0.5
4      S02 1.
5      XANES      3.7 0.05      0.1
6      FMS 7
7
8      POTENTIALS
9      0      79      Au      -1      -1      0.
10     1      79      Au      -1      -1      0.

```

Running the 91 simulations (one for each of the distorted structure) takes approximately 30 minutes. Were we to generate thousands more or employ RMC or MD, this process could take weeks of compute time. We plot the resulting XANES spectra from the FEFF simulations in figure 2.2.

2.2 Generating Disorder via Probability Distribution Averaging

One way to characterize system disorder is with the Gaussian width, σ , of the partial radial distribution function. The idea of our statistical averaging method is to emulate this width by weighting the simulated XANES spectra accordingly. For example, Figure 2.3 depicts a histogram with $\sigma = 0.1$ Å. Each histogram bin represents a simulated XANES spectrum with a different isotropic displacement. For example, the bin at $\Delta\rho = 0.0$ Å represents the simulated XANES spectrum with no distortion, and the bin at $\Delta\rho = -0.2$ Å represents the simulated XANES spectrum with all the atomic coordinates shifted isotropically inwards towards the center absorber by 0.2 Å. The height of each bin, $f(\Delta\rho)$, represents the relative contribution of each simulated XANES spectrum towards the resulting weighted spectrum. For visual clarity, Figure 2.3 depicts only 40 bins; the actual weighting includes 91 bins ranging from -0.45 Å to $+0.45$ Å.

The disordered, gaussian-averaged XANES spectrum, $\langle\mu(E)\rangle$, using the histogram weighting of the gaussian in Figure 2.3 is calculate via Equation (2.1):

$$\langle\mu(E)\rangle = \frac{1}{S} \sum_{\Delta\rho=-.45}^{+.45} g(\Delta\rho \mid \mu = 0, \sigma = 0.1) \mu(E \mid \Delta\rho) \quad (2.1)$$

In the above equation, $\Delta\rho$ is the isotropic, radial displacement of each atom from its original position, and $\mu(E \mid \Delta\rho)$ is the simulated FEFF spectrum for the given $\Delta\rho$ configuration. Furthermore, in Equation (2.1), S represents a standardization factor needed to negate the effect of the changing Gaussian height as a function of the variance, σ^2 . With the inclusion

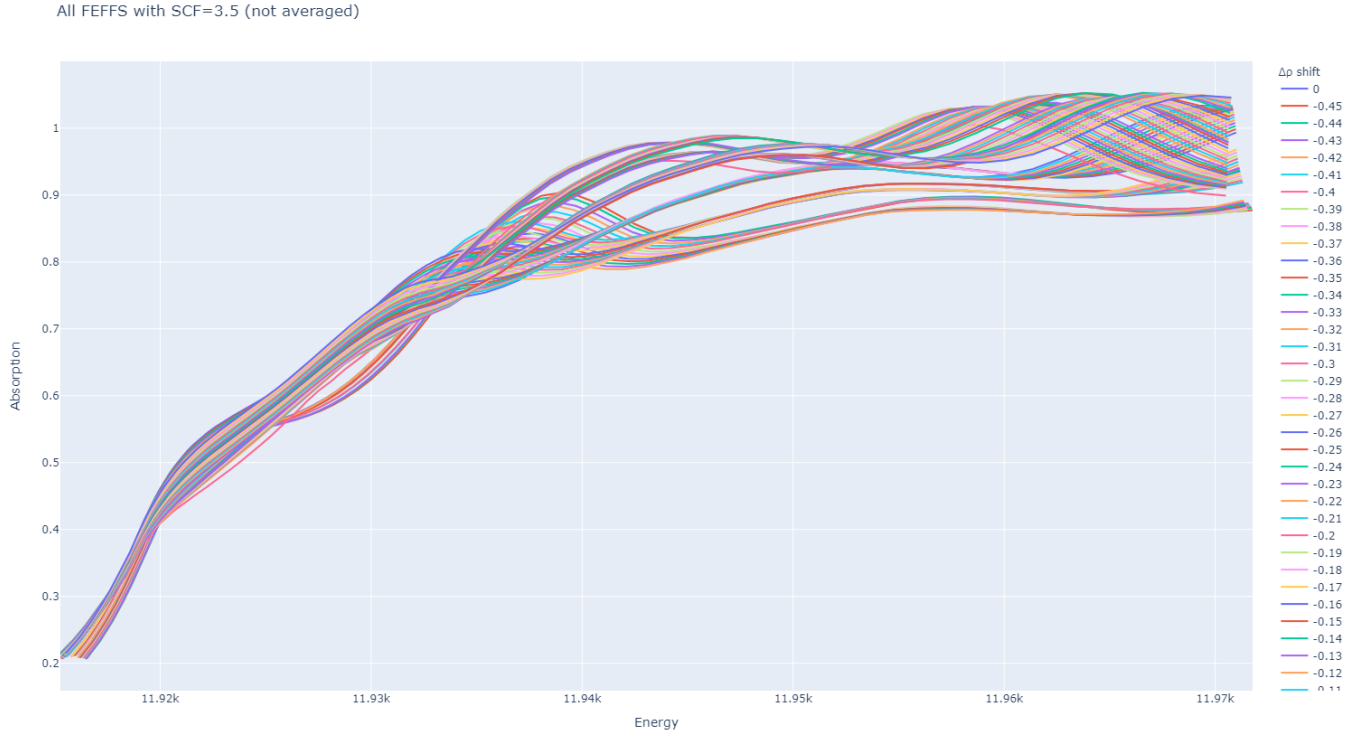


Figure 2.2:

TEMPORARY - way too much info. I'll select a few.

Each spectrum represents the FEFF simulation results for a different distorted structure. For each spectrum, the crystal structure and center absorber remain constant, the only parameter that varies is the euclidean distance from the center to the other coordinates.

of S , only the relative heights of each bin matters for producing the averaged XANES spectrum. This standardization factor is defined in Equation (2.2):

$$S = \sum_{\Delta\rho=-.45}^{+.45} g(\Delta\rho \mid \mu = 0, \sigma = 0.01) \quad (2.2)$$

In both equations (2.1) and (2.2), the function g is just the typical Gaussian distribution probability density function (Equation 2.3):

$$g(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2} \quad (2.3)$$

The above example only generates one (simulated) disordered XANES spectrum and does so via weighting of a Gaussian distribution with mean and variance equal to 0 and 0.01, respectively. To simulate systems with different degrees of disorder, we can vary the

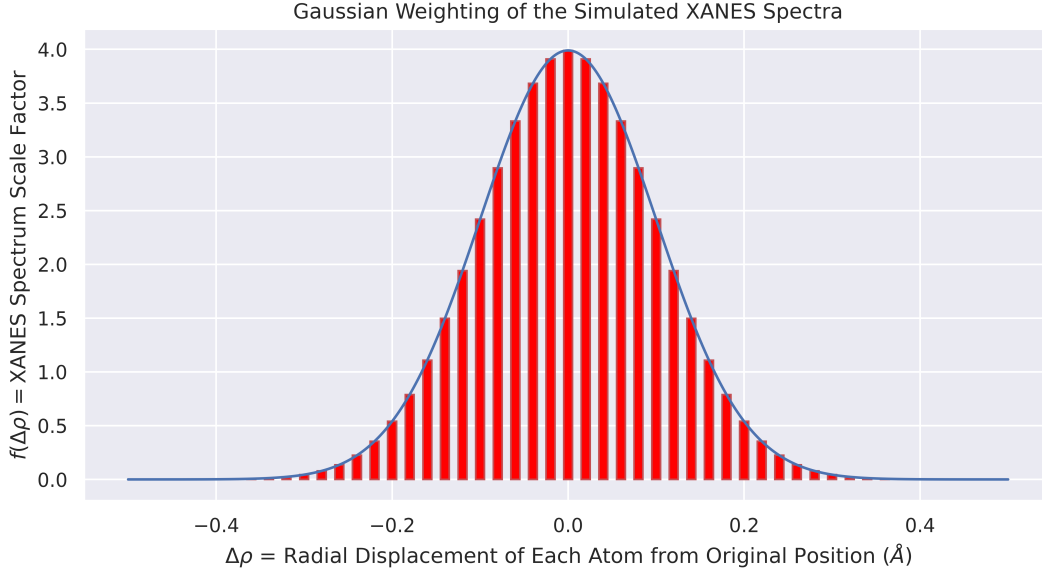


Figure 2.3: A Gaussian distribution probability density function can be used to calculate the relative weight of each FEFF generated XANES spectrum towards one simulated, disordered spectrum. Each bin (red bar) represents a FEFF generated spectrum; the x -axis is the isotropic shift of the atomic positions, and the y -axis is the relative weight factor.

shape of the probability density function. With a Gaussian distribution, we can only vary the mean and variance; to simulate even more conditions, however, we can instead use the multivariate skew-normal distribution (2.4) [11, 12], $f(x)$.

$$f(x) = 2\phi(x)\Phi(\alpha x) \quad (2.4)$$

where $\phi(x)$ is the Gaussian PDF:

$$\phi(x) = \frac{1}{\sqrt{2\pi}} e^{-\frac{x^2}{2}} \quad (2.5)$$

and $\Phi(x)$ is the Gaussian CDF:

$$\Phi(x) = \int_{-\infty}^x \phi(t) dt \quad (2.6)$$

Equation (2.4) includes the shape parameter, α , which has the nice property of producing a right-skewed distribution when positive and a left-skewed distribution when negative. When $\alpha = 0$, the distribution simply produces the typical Gaussian distribution (eq. 2.3). Utilizing equation (2.4), we can vary μ , σ , and α to alter the first four moments of the function: mean, standard deviation, skew, and kurtosis. Eighteen possible skew-norm weighting functions are

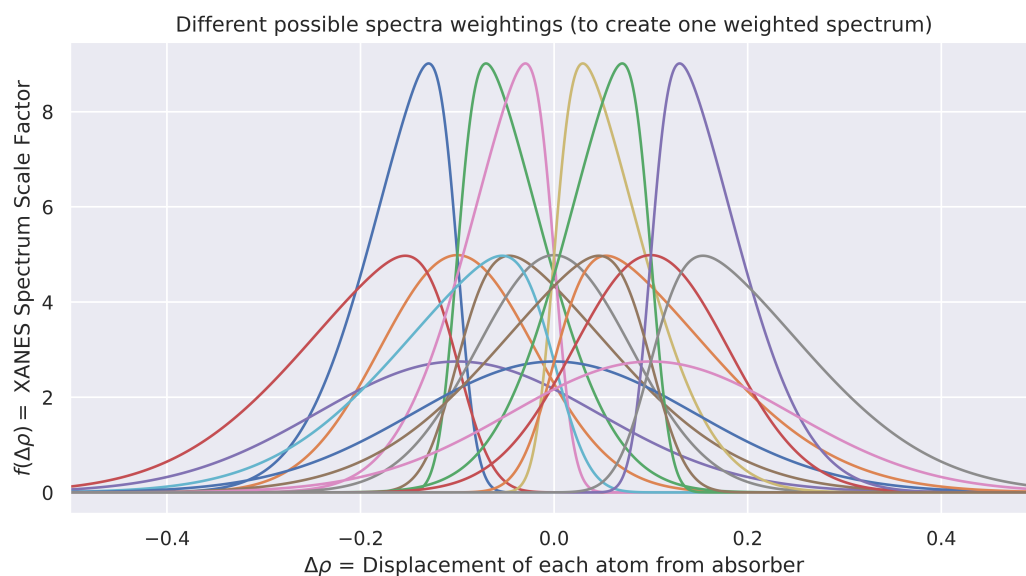


Figure 2.4: Eighteen skew-normal distributions plotted with all possible combinations of $\sigma = \{.08, .145\}$, $\mu = \{-.1, 0, .1\}$, and $\alpha = \{-5, 0, 5\}$. Each represents a possible way to produce a simulated, disordered spectrum from many FEFF-simulated, distorted spectra

plotted in Figure 2.4. To produce the neural network training data, 1000 such weightings are used.

The disorder of the skew-normal generated, disordered spectrum is characterized by the mean squared displacement of each atom from its original position ($\Delta\rho$), weighted in the same manner as the spectra.

Instead of characterizing the disordered spectrum by the standard deviation of the gaussian used to create it

The weighted mean squared displacement, MSD , is calculated via equation (2.7):

$$MSD = \frac{1}{S} \sum_{\Delta\rho=-.45}^{+.45} f(\Delta\rho | \mu, \sigma^2, \alpha) \quad (2.7)$$

Here, $f(x)$ is the skew-normal function from equation (2.4), and the MSD of each individual FEFF spectrum is equal to the isotropic distortion, $\Delta\rho$.

2.3 Simulation vs. Experimental Data

To check our FEFF simulation parameters, as well as the validity of the gaussian-weighted disorder technique, we compare the simulation data to experimental data. In Figure 2.5, both experimental and simulation spectra for bulk-like and nanoparticle scenarios are plotted.

Can someone give me citations for these?

EXAFS fitting was used to characterize the disorder in the experimental measurements. For the bulk foil, this parameter was found to be $\sigma^2 = 0.0081(5) \text{ \AA}^2$, and for the 8 nm disordered particle, $\sigma^2 = 0.0102(8) \text{ \AA}^2$. One simulated, disordered spectrum was weighted according to the gaussian $N(0, 0.09)$ to represent the disordered nanoparticle, and the other was weighted according to the gaussian $N(0, 0.038)$ to represent the bulk. These weightings correspond to MSD values that match the measured σ^2 values for the experimental data.

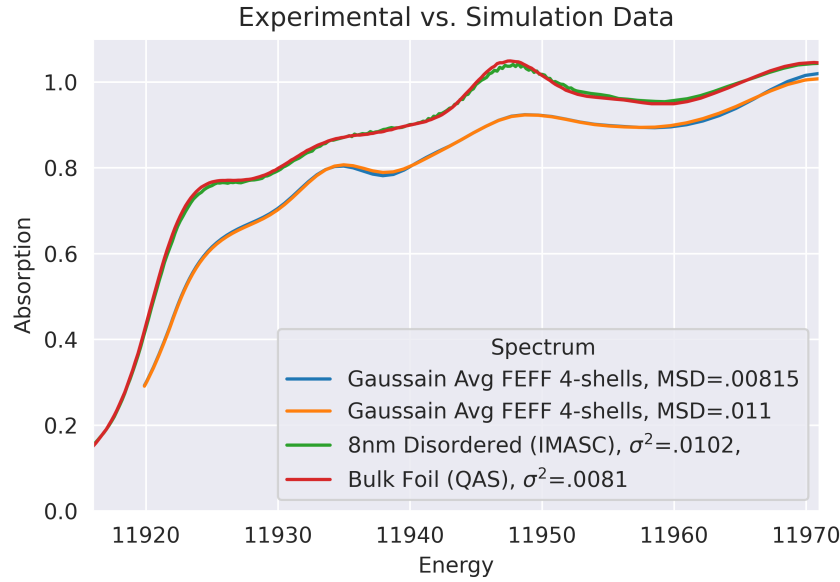


Figure 2.5: Comparing the bulk foil (red) measurement to the 8 nm disordered nanoparticle (green) measurement is an analog to comparing the simulated, non disordered FEFF spectrum (blue) to the simulated disordered spectrum (orange).

In Figure 2.5, the bulk Au foil spectrum is above the 8 nm nanoparticle spectrum (more absorption) until the peak around 11937 eV, where the NP absorption becomes higher. The two criss-cross again over the next two peaks, changing which material has the higher absorbance in an energy range. This change is more easily seen in Figure 2.6, which plots the difference between the the bulk material and the nanoparticle absorption for both the experimental measurements and the simulations. The experimental and simulation difference-spectra follow the same trend with the exception of the peak around 11947 eV.

Figures 2.5 and 2.6 aren't meant to be perfect comparisons of simulations vs. experimental data. For one, the experimental data compares a bulk spectrum to a nanoparticle. By contrast, both the simulation spectra are of the same size 55 atom cluster. Still, much of the disorder trends are coded in the simulation approach.

To test if the size information is also coded in our simulations, we compare different size simulations to experimental data in Figure 2.8. As expected, including more atoms in the simulation produces more bulk-like spectrum characteristics, such as larger amplitude peaks.

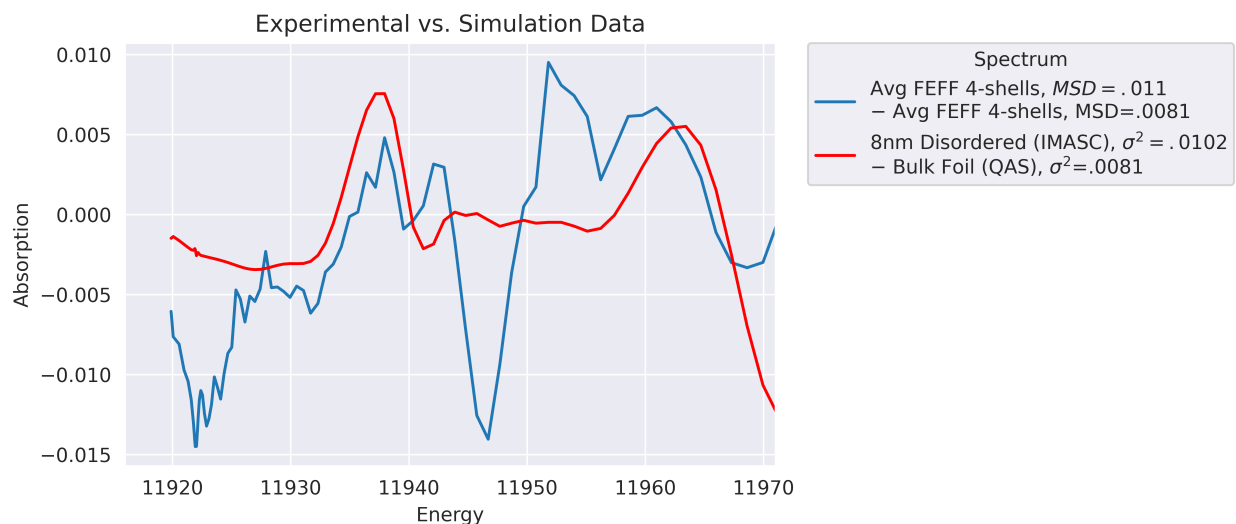


Figure 2.6: The difference between the nanoparticle spectrum and the bulk spectrum are plotted for the same data as in Figure 2.5. It is easier to see where the bulk and the nanoparticle absorption crisscross by plotting the difference.

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2.4 Particle-Averaged FEFF Simulated Disordered Structures

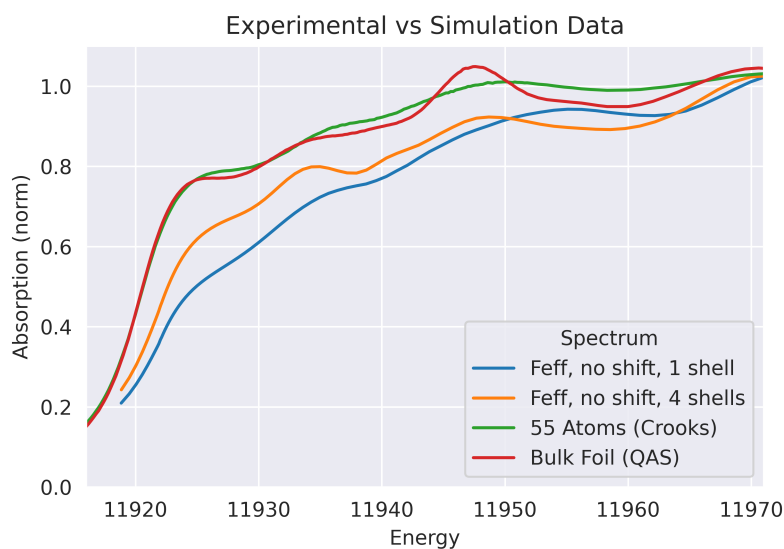


Figure 2.7: Comparing the bulk foil (red) measurement to the 55 atom nanoparticle (green) measurement is an analog to comparing the 13 atom simulated spectrum (blue) to the 55 atom simulated spectrum (orange).

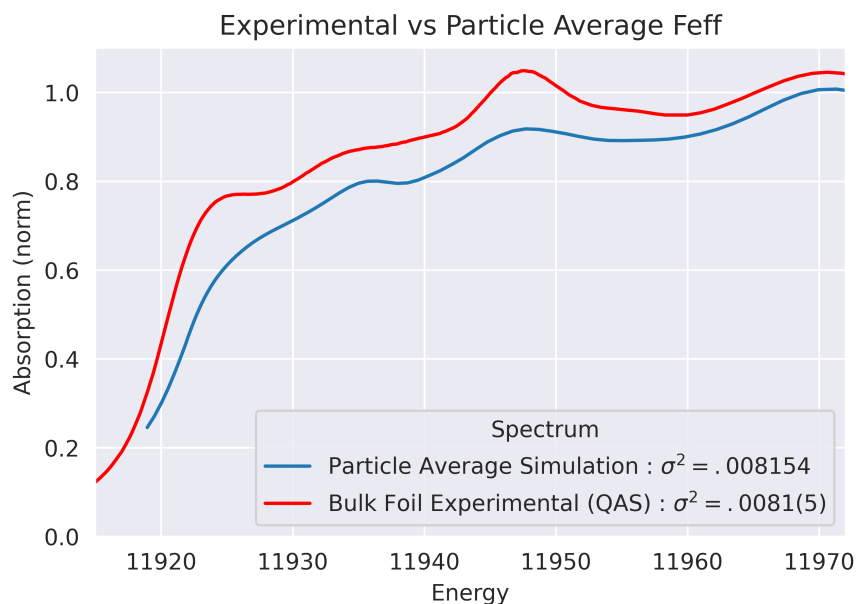


Figure 2.8: Comparing the bulk foil (red) measurement to a simulated large, bulk-like nanoparticle with the same disorder. The FEFF-

Chapter 3

Machine Learning

An explanation of Machine Learning and Neural Networks in general

3.1 Autoencoders if they become useful

Talk about how autoencoders work. Give a nice broad explanation and really go into the math. Include some nice diagrams

Here's [13] a good source to read and model off of. Here [14] is another paper that might be interesting to read. It's about getting noise-free data from the original data using an autoencoder. Neat idea, and could actually be very relevant because they're using geophysical data.

Chapter 4

Results

Here I expect to showcase lots of nice figures and data to show how well the neural network works

4.1 temp

Appendix A

An appendix

Appendices are a good idea for almost any thesis. Your main thesis body will likely contain perhaps 40-60 pages of text and figures. You may well write a larger document than this, but chances are that some of the information contained therein, while important, does *not* merit a place in the main body of the document. This sort of content - peripheral clarifying details, computer code, information of use to future students but not critical to understanding your work ... - should be allocated to one or several appendices.

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