Signal processing using wavelet transforms for electron spin resonance spectra

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Abstract

Electron spin resonance (ESR) spectroscopy is a field of study in Chemistry that analyzes unpaired electrons in molecules. Spectra signals, the medium for that analysis, are often distorted and obscured by noise. Wavelet-based denoising methods aim to improve clarity while retaining spectral features. The Noise Excision via Recursive Deconvolution (NERD) software, hosted by Cornell University, is an innovative tool for wavelet-based denoising, compatible with objective approaches to denoising spectra. This research applied the software subjectively, in a way that is susceptible to bias and over-processing without accuracy checks. Objective approaches, based on Srivastava’s work and further developed in this project, attempt to improve denoising effectiveness and eliminate bias. The goal of this project is to create an in-depth understanding of the mathematical foundations of ESR denoising, communicate it to others, and use it to compare subjective and objective approaches of denoising ESR spectra. Also, this research aims to explore potential methods for spectral analysis and coupling constant determination. The NERD software was used for subjective wavelet thresholding; an objective wavelet decomposition method was developed using Srivastava’s groundwork of finding threshold bounds and optimal decomposition levels. Additionally, continuous wavelet transform (CWT) heat maps were analyzed for their potential in ESR spectral analysis and coupling constant determination. Successful denoising was achieved for specific datasets; however, since accurate spectra signals are unknown, our accuracy remains unknown until viable accuracy checks are developed in a later stage of this research. While a universally valid denoising method was not achieved, this project revealed the strengths and limitations of the approaches used in this research. This project also contributes to current research into viable denoising tools, free from bias, and coupling constant extraction methods in ESR spectroscopy.

Background Information

The purpose of this research is to denoise electron spin resonance (ESR) spectra signals and obtain coupling constants using wavelet transforms. ESR spectroscopy is a subset of spectroscopy that examines paramagnetic species (molecules containing unpaired electrons) using microwaves in the presence of a magnetic field. “When an external magnetic field is applied, the energy levels associated with different spin orientations of the unpaired electrons split, resulting in distinct energy transitions.” (BYJU'S, n.d.). ESR spectroscopy has applications in material science and biology, such as the study of electrons in various complexes, xenobiotics, and free radicals (JEOL Ltd., n.d.).

Figure 1: The JEOL X-310 ESR spectrometer detected electron spin resonance by measuring microwave absorption derivative signals under a magnetic field sweep. This spectrometer model was used in collecting ESR data for this research. (JEOL Ltd., n.d.).

A significant obstacle to these applications and the general field of spectroscopy is the presence of noise in recorded spectra. Noise is understood to be the unwanted interference against a desired signal. Causes of noise in ESR spectroscopy include environmental electromagnetic interference, thermal fluctuations of electronics, shot noise from electrical junction crossings of charged particles, and low-frequency $\frac{1}{f}$ noise (SPIE, n.d.). In ESR spectroscopy, noise can distort and obscure spectral information, causing measured spectra values to deviate from the actual signal. For this reason, denoising techniques that improve spectral clarity while retaining signal data are essential for interpreting noisy ESR spectra.

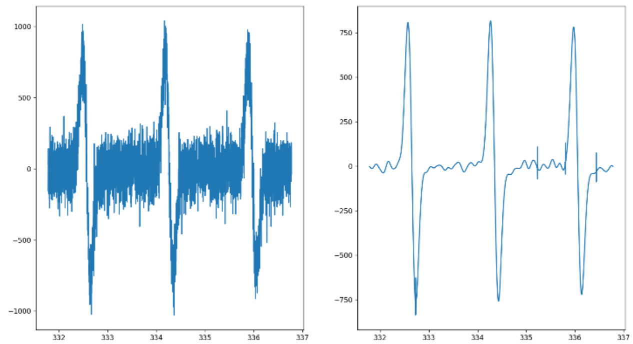


Figure 2: This figure compares the noisy ESR spectrum shown on the left, which reveals deviations that obscure the signal, and the denoised version of that same spectrum shown on the right using a wavelet-based denoising method explained further in this report.

This paper focuses on denoising and interpretation of ESR spectra; a complete coverage of all aspects of ESR spectroscopy is beyond its scope. This project builds off Dr. Madhur Srivastava's research on wavelet-based denoising and coupling constants determination. A major resource for this project was the NERD software, developed by the Advanced ESR Technology (ACERT) center in collaboration with the Cornell Center for Advanced Computing (CAC), which acts as a specialized tool for wavelet-based denoising and spectral analysis (Cornell University, n.d.). Existing denoising methods and software provide a foundation for interpreting noisy ESR spectra; this project aims to develop objective denoising methods and apply them to interpret ESR spectra provided by Chemistry professor Dr. Sipe from Hampden-Sydney College.

Foundations of ESR Signal Processing

This report provides an overview of the mathematical foundations directly relevant to ESR spectra processing. Detailed derivations and advanced linear algebra principles behind Fourier analysis and wavelet transforms will not be covered; all references to these math concepts are based on *A First Course in Wavelets with Fourier Analysis* by Albert Boggess and Francis J. Narcowich (Boggess & Narcowich, 2009). Half of the research period was spent learning the mathematical foundations of wavelets, using this book as the primary source. The following section describes the principles of Fourier transforms and the rationale behind the use of wavelets for processing ESR spectra, and how Dr. Srivastava influenced this research.

The Fourier transform decomposes a signal into its sinusoidal components at different frequencies. Since the transformation is invertible, after frequency components are processed, the components can be reconstructed into a processed signal. Fourier transform processing targets specific features of a signal, based off frequency, unlike indiscriminate methods like signal averaging, which affects all data equally. Signals whose statistical characteristics are not changing are known as stationary signals. A Fourier transform is a powerful tool for processing such signals, but it is not as effective for signals whose frequency features change over time, such as noisy ESR spectra (Sahoo & Srivastava). The results of a couple of Fourier denoising problems studied during the foundations period of the research are displayed below.

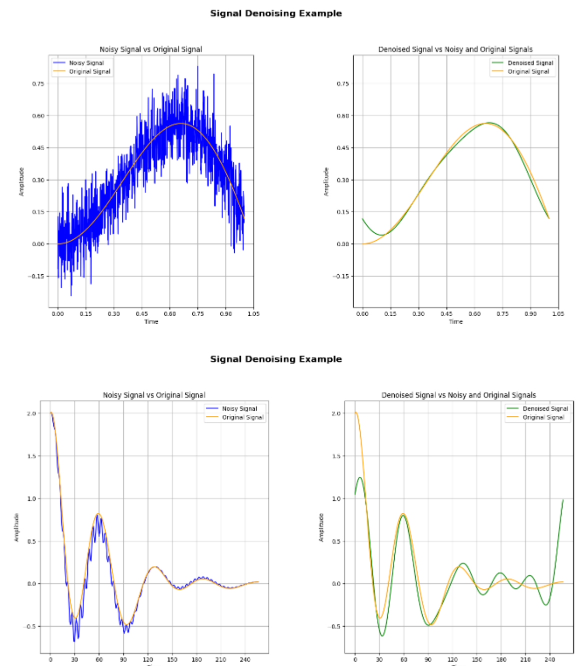


Figure 3a-b: Examples of denoising using the Fourier transform in Python are displayed in this figure. Each plot shows a noisy signal in blue, the original signal in orange, and the denoised signal in green. Denoising is conducted by filtering low-magnitude frequency components. These examples show the strengths and limitations of denoising signals under the Fourier transform.

One way to surpass the non-stationary limitation of the Fourier transform is the wavelet transform, which analyzes both time and frequency. This is done by using a wavelet, a function with specific mathematical properties, to capture changes in a signal through a scaling parameter (related to frequency) and a translation parameter (related to time). A wavelet transform provides detailed information about a signal's features in the form of wavelet coefficients, which can be thresholded, making it ideal for denoising ESR spectra. Due to how the wavelet interacts with the signal, coefficients with large magnitude values tend to represent the proper signal, while smaller coefficients are most likely noise. The wavelet transform can be implemented in both continuous and discrete forms. Both approaches were applied utilizing Srivastava's continuous wavelet transform (CWT) code for heat maps, and the stationary/decimated wavelet transform (SWT/DWT) used in the NERD software for signal decomposition. Data processing on the NERD software involved two operations. They are windowing, where information outside magnetic field strength interval(s) is discarded, and thresholding, where wavelet coefficients within two threshold bounds are zeroed out. Windowing and thresholding were the primary methods of signal processing for this project. Understanding these principles and Srivastava's contributions was therefore central to this research.

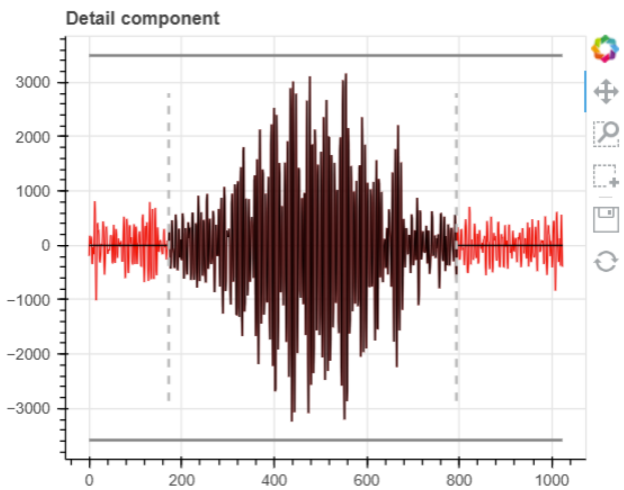


Figure 4a: This figure displays the windowing tool provided by the NERD software, capable of isolating intervals of signal from being zeroed out; the processed signal is in black, and the original signal is in red.

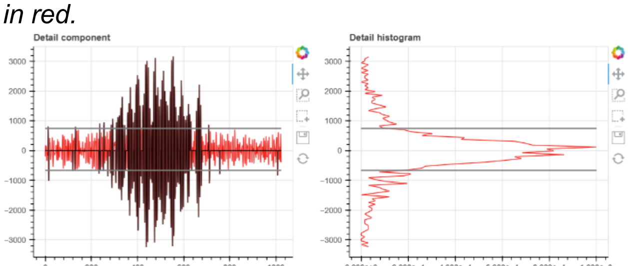


Figure 4b: This figure displays the thresholding tool provided by the NERD software, capable of zeroing wavelet coefficients between the threshold bounds in the detail component distribution histogram; the processed signal is in black, and the original signal is in red.

Srivastava's work on denoising ESR spectra, particularly his technique for optimal decomposition level selection, influenced our methodology significantly. Using wavelet transform decomposition, like the NERD software does, spectra can be separated into approximation and detail components at differing resolution levels. The number of resolution levels is dependent on a logarithm with base two of the data file length. One aspect of Srivastava's influence was the use of sparsity change when selecting the optimal decomposition level. This is vital because processing a signal with high decomposition levels can result in heavy information loss. In this context, a sparse wavelet coefficient distribution is one in which most coefficients are close to zero. Sparsity change plots expose abrupt transitions from noisy to noise-free detail component, which helps reveal the cut-off for the maximum decomposition level (Bekerman & Srivastava, 2021).

Srivastava provided a method for finding threshold bounds through statistically analyzing spectral signals. His method revolves around sparsity calculations of the detail coefficients at different decomposition levels. It applies three main criteria that thresholds based on sparsity. This process is repeated for the following decomposition levels until the optimal decomposition level (Srivastava, Anderson, & Freed, A New Wavelet Denoising Method for Selecting Decomposition Levels and Noise Thresholds, 2016):

1. When the sparsity value is less than 0.01, all the coefficients are removed. These coefficients are assumed to be dominated by noise
2. When the sparsity value is between 0.01 and 0.2, threshold bounds are determined through statistical calculations outlined by Srivastava
3. When the sparsity value is greater than 0.2, threshold bounds are set to zero, as the actual signal theoretically dominates these coefficients

An additional method by Srivastava extracts hyperfine and super-hyperfine components of ESR spectra for analysis and coupling constant determination (Roy & Srivastava, 2022). By selecting an appropriate decomposition level, signal features at a specific resolution can be extracted. The hyperfine component is obtained by discarding higher frequency information, which can be implemented by zeroing the detail components up to the optimal decomposition level before reconstruction. In contrast, the super-hyperfine component is obtained by discarding the lower frequency information, which was achieved by zeroing the approximation component up to the optimal decomposition before reconstruction. These frequency-dependent components can be analyzed, and coupling constants can be determined. The ESR theory behind this method is complex and not fully explored in this project. Nevertheless, the capabilities of wavelet decomposition to isolate features of a signal are acknowledged.

Materials and Methods

Software and Tools

Signal processing and Srivastava's decomposition level and thresholding approaches required computational tools. This project used the Python programming language, Cornell's NERD software, and ESR spectra provided by Dr. Sipe. The PyWavelets, NumPy, and Matplotlib are primary Python packages used in this project's coding. Relevant Scripts, such as thresholding_bounds, decomposition_level_selection, automated_threshold_bounds, and Srivastava's cwt_heat_map, were used for thresholding, optimal decomposition level selection, and analysis of wavelet coefficients.

Data Source

The data used in this project consisted primarily of .txt files provided by Dr. Sipe obtained from an ESR spectrometer. Each file contained a single column of information. The initial seventy-nine rows gave experiment descriptions. The descriptions include x-axis units (milliTesla), y-axis units (generic amplitude), x-range, y-range, file length, real and imaginary-component length, and sampling mode. Following the descriptions, there were rows of real-component measurements of the derivative of the absorption signal whose length was always a power of two. The imaginary component data, identical in length to the real component, was separated from the real component data set by an indication row.

Data Preparation

Data files were imported into Python via NumPy library functions. All data files provided by Dr. Sipe were reformatted to contain two columns of purely numerical information, separated by commas, making them compatible with the NERD software and suitable for processing. The first column corresponds to the magnetic field strength measurements, and values in the second column contain the absorption signal derivative values. All imaginary-component values from ESR spectra were ignored.

Data Processing

Reformatted files were uploaded to the NERD software and analyzed using the Daubechies 6 or Coiflet 3 wavelet under the undecimated parameter. For discrete wavelet processing, the Daubechies 6 and Coiflet 3 wavelets were applied, while the complex Morlet wavelet was necessary for continuous wavelet processing. Data processing, especially done in the NERD software, involved subjective windowing and thresholding. At this stage of the research, approximation components were not windowed or thresholded out of concern for excessive loss of signal information.

The optimal decomposition levels for all ESR spectra were determined by using Srivastava's optimal decomposition selection code; a sparsity change graph at given decomposition levels was added to this code for additional analysis. After processing, the NERD software reconstructed signals to be subjected to analysis. Srivastava's approach to determining hyperfine and super-hyperfine coupling components, outlined in the **Foundations of ESR Signal Processing** section, was also attempted. Reformatted data files were entered into the CWT heat map code for producing a potential coupling constant determination method, with reference values provided by Dr. Sipe.

An automated denoising code was developed in Python to create an objective method for denoising ESR spectra. This code builds on principles influenced by Srivastava's methods. The main script accepts ESR data and wavelet type as inputs, reads the data, computes the wavelet decomposition using the stationary wavelet transform (SWT), and processes the signal up to an optimal decomposition level determined by Srivastava's decomposition_level_selection script. At each decomposition level, the thresholding_bounds script calculates threshold bounds based on statistical properties of the wavelet coefficients, as outlined in the **Foundations of ESR Signal Processing** section. Coefficients within the threshold bounds, presumed to be noise dominant, are zeroed, while signal-dominant coefficients are retained. The denoised signal is then reconstructed using the inverse stationary wavelet transform (ISWT). The automated denoising code outputs the denoised signal saved in the two-column format, side-by-side plots of the original and denoised signals, and the computed threshold parameters. No objective method for determining the accuracy of denoised ESR spectra was fully developed in this project. This automated approach complements the procedure of the NERD software and Srivastava's methods for denoising ESR spectra.

Results

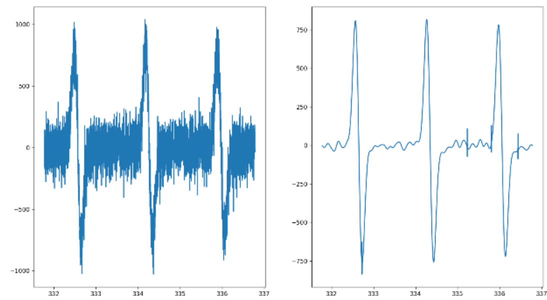


Figure 5: Denoising of TEMPO 4k 50 μM 100-scan data using the automated threshold bounds method is shown in this figure. The original spectra are shown on the left, and the denoised spectra is shown on the right.

The denoised signal in Figure 5 shows distinct peaks representative of the true signal, while the apparent high-amplitude noise is suppressed. This data set is simple and resistant to over-processing.

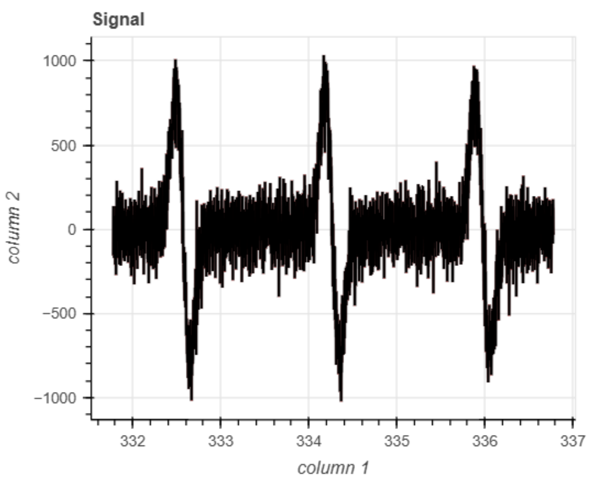


Figure 6: Original ESR spectra of TEMPO 4k 50 μM 100-scan data.

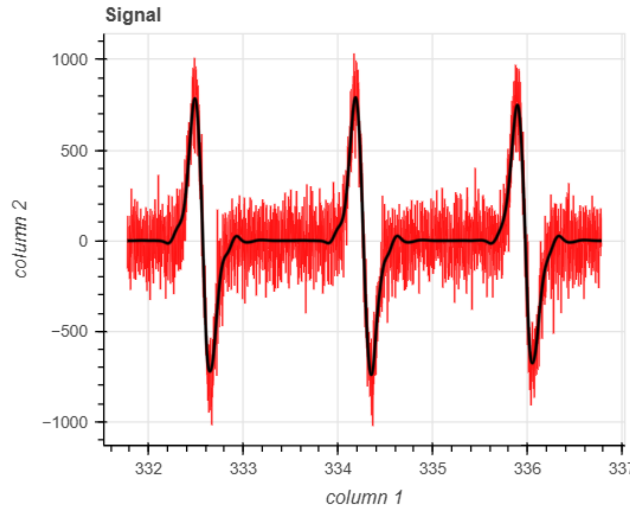
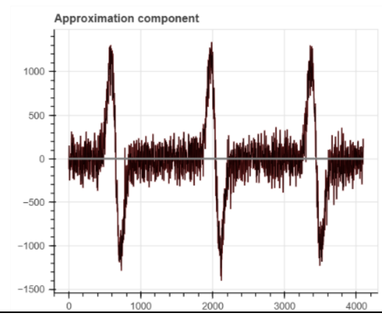
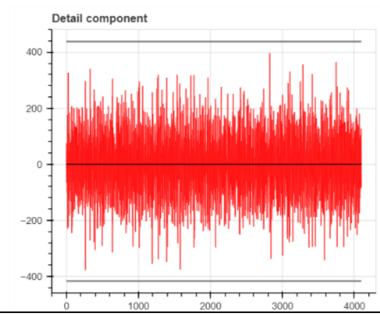
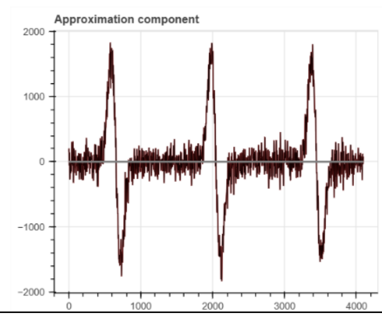
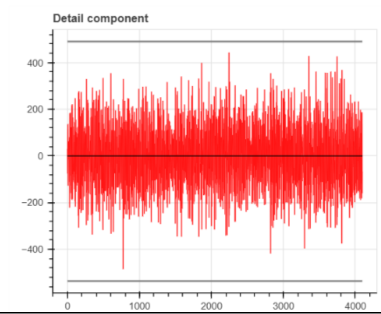
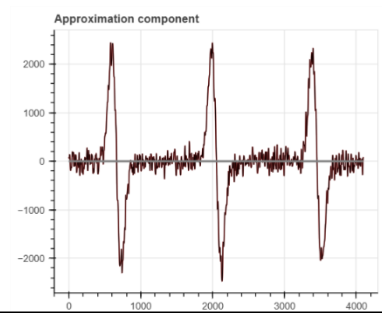
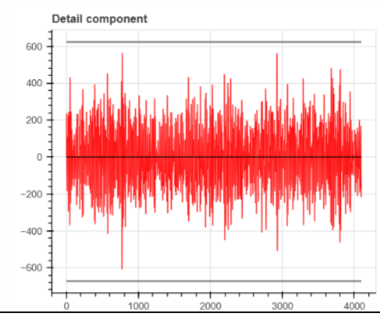
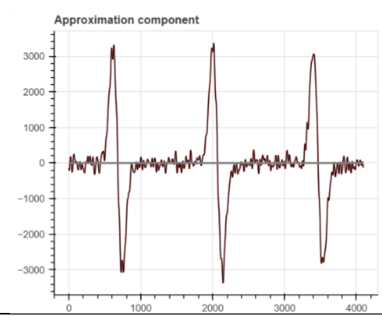
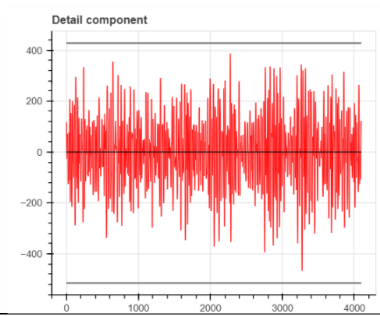


Figure 7: Denoising of TEMPO 4k 50 μM 100-scan data using subjective processing in the NERD software is shown in this figure. The denoised spectrum is shown in black, and the original spectrum is shown in red. This figure shows the reconstruction following the processing applied in Figure 8.

The result of subjective denoising, as revealed by Figure 7 in comparison to Figure 5, implies over-processing, as the spectrum of Figure 8 is terrifyingly smooth with a noticeable loss of signal intensity. However, it is impossible to say for sure if this spectrum is over- or under-processed without an accuracy indicator for the actual signal.

Wavelet Transform info:

- Coif3 wavelet type
- Optimal decomposition level 6

Level	Approximation	Detail	Rationale for Subjective Processing
1			The Level 1 detail component was thresholded harshly. This level typically contains noise for the data used in this research, so the component is completely zeroed.
2			Like the previous level, the detail histogram is not very sparse. Detail wavelet coefficient distribution so that the whole component is zeroed.
3			Like the previous Level, the whole detail component is zeroed out.
4			Like the previous Level, the whole detail component is zeroed out.

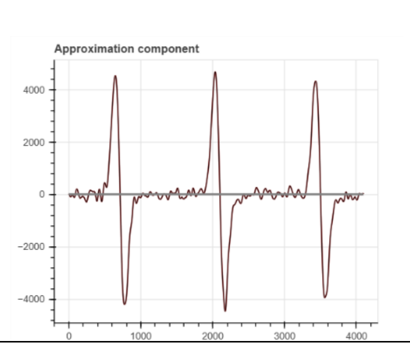
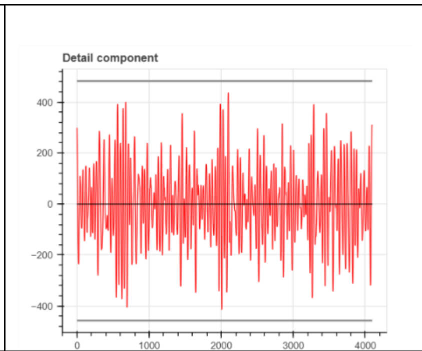
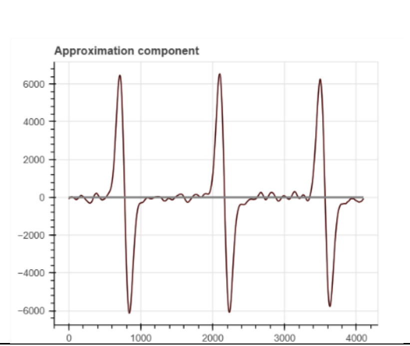
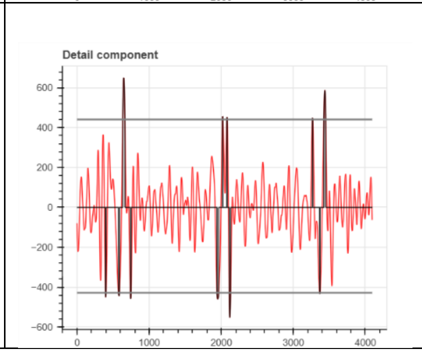
5			Like the previous Level, the whole detail component is zeroed out.
6			The wavelet coefficient distribution is sparser than the previous levels, though not yet very sparse. Thus, the detail component was subjected to a strong thresholding, but less severe than the previous level.

Figure 8: This table outlines my initial approach and reasoning for thresholding of the TEMPO 4k 50 μM 100-scan data at each decomposition level in the NERD software, up to the optimal decomposition level determined by Srivastava's code.

The rationale for subjective thresholding is susceptible to bias, especially when dealing with different data types. Data types with certain wavelet coefficient distributions may suggest that noise is dominant throughout levels or specific wavelet coefficients. However, a dataset can contain complex features that resemble noise via abrupt changes. The wavelet coefficient distributions could instead indicate signal-dominant coefficients and are susceptible to over-processing to the subjective eye. One way to combat this is window thresholding, but isolating intervals of true signals from processing is challenging, especially when the actual signal is unknown.

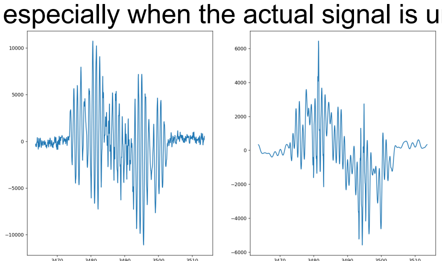


Figure 9: The denoising of N15 Guanosine data using the automated threshold bounds method is shown in this figure. The original spectrum is shown on the left, and the denoised spectrum is shown on the right.

N15 guanosine provides a complicated spectrum that is difficult to denoise in general. Figure 9 serves as a great example of a dataset type that does not adhere to Srivastava's objective approach to optimal decomposition level selection. Apparent information loss occurred because the code selected an excessively high decomposition level for processing.

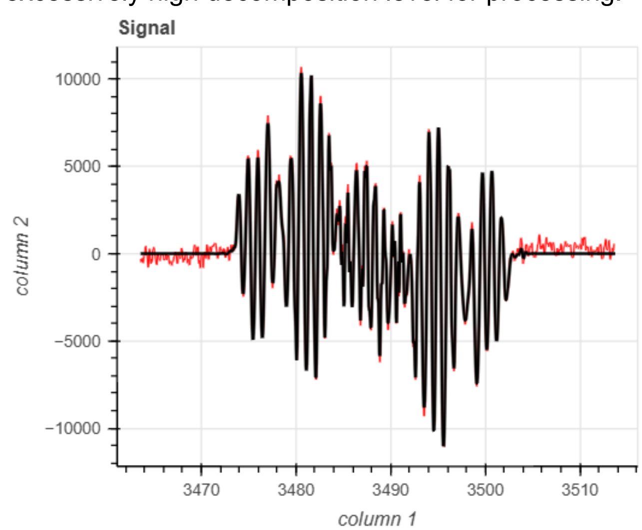


Figure 10: This figure shows the denoising of N15 Guanosine data using subjective processing in the NERD software. The denoised spectrum is shown in black, and the original spectrum is shown in red.

A more conservative approach to subjective denoising, compared to the previous simple spectra, was applied to this spectrum. Not as much intensity was lost, and the beginning and end of the actual signal are potentially revealed in the denoised spectra.

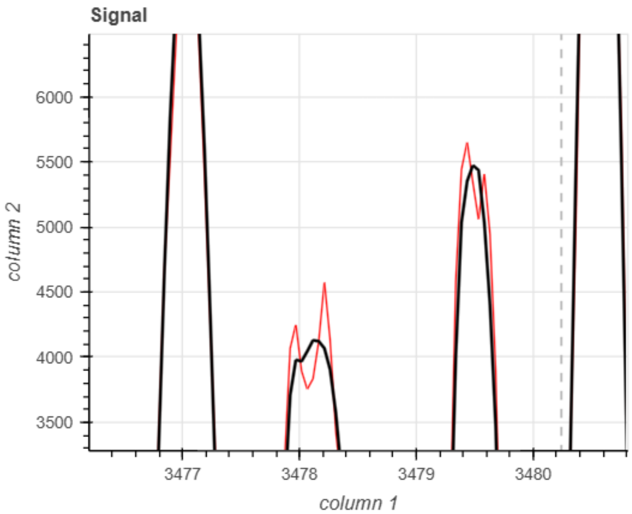


Figure 11: Zoomed-in version of Figure 10.

This zoomed-in version of Figure 10 reveals a smoothing of the jagged features in the middle of the noisy spectra. These jagged features could be part of the actual signal or mostly noise.

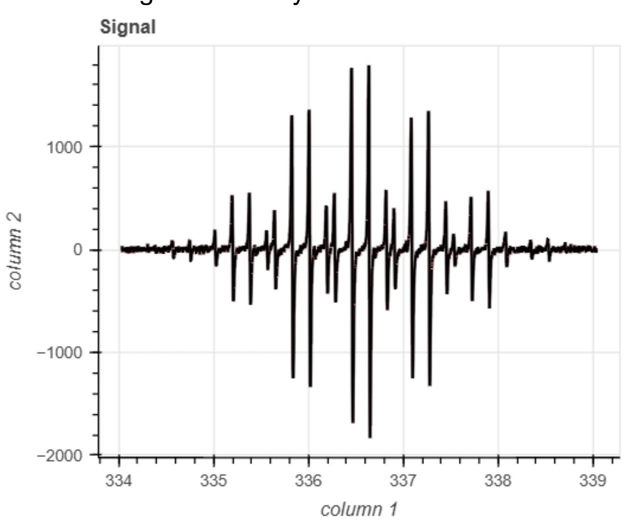


Figure 12: Original ESR spectra of Phenalenyl data.

Various distances between high-intensity coefficient pillars on this heat map reveal the spectrum's coupling constants. These wavelet coefficient patterns are not easy to interpret. CWT heat maps have potential in the sector of coupling constant extraction if paired with a method that recognizes patterns with intensity in wavelet coefficients.

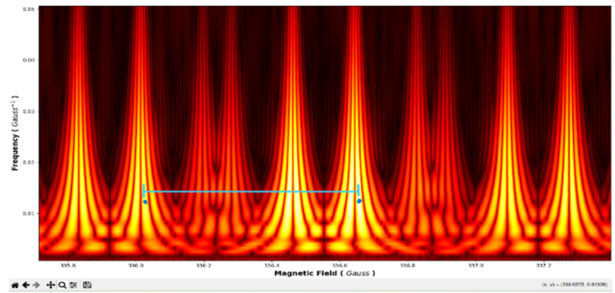


Figure 13: This figure shows the CWT heat map of the Phenalenyl data represented in Figure 12. Coupling constant: 6H @ 6.29 Gauss. The horizontal blue line in the figure corresponds to 0.6285 mT in magnetic field strength. The blue dots indicate the estimated location of the maximum intensity on the heat map; exact x-values were recorded based on the cursor position.

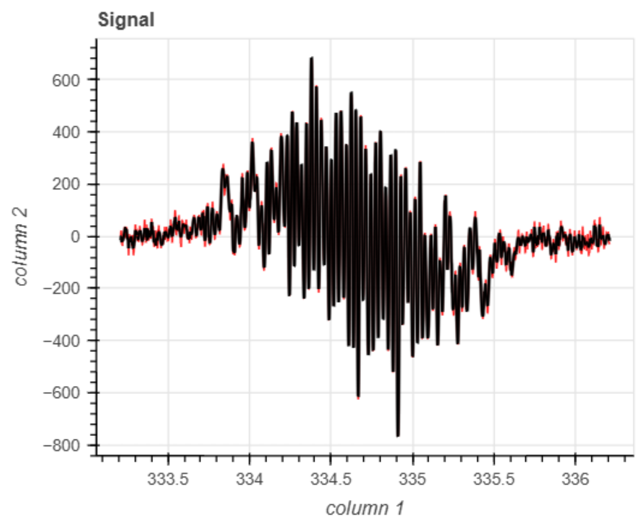


Figure 14: Denoising of Curcumin data using subjective processing in the NERD software is displayed in this figure. The denoised spectrum is shown in black, and the original spectrum is shown in red.

This spectrum has complex features that make it exceedingly challenging to denoise and extract coupling constants.

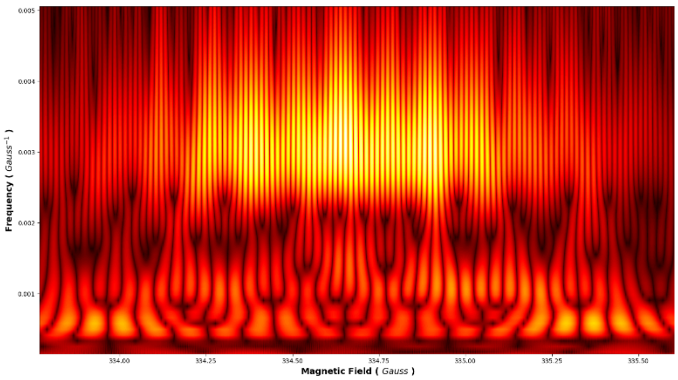


Figure 15: The figure displays the CWT heat map of Curcumin data represented in Figure 14. Magnetic field strength is measured in mT.

Patterns are very recognizable in this heat map, but they could not be interpreted along with coupling constants during this research.

Discussion

The results of this project reveal the utility and limitations of the tools and methods used in this project. The NERD software proved to help explore subjective thresholding, windowing, and reconstruction of ESR spectra. However, when one does not know the features of the actual spectra signal, subjective processing can only get you so far. Similarly, the automated denoising code developed in Python did not perform as well as I hoped, and no objective method was used during this research to determine the accuracy of the denoised spectra. Srivastava's decomposition level selection code often produced very high optimal decomposition levels for much of our data; processing at these levels oversimplified the reconstructed signals instead of capturing spectral features. One promising result was the CWT heat maps, as they contained substantive information that has potential for estimating coupling constants of noisy ESR spectra. This suggests a clear avenue for future work, where further research could explore methods for utilizing the CWT heat map for spectral analysis and determining coupling constants.

Subjective spectra processing using wavelet decomposition or subjective use of the NERD software can be effective if one knows what they are looking for. Many wavelet coefficients, including some representing the proper signal, were thresholded in my initial denoising, as seen in Figure 7. The figure appears suspiciously smooth and may have been over-processed. Similarly, in Figure 11, the zoomed-in version of Figure 10, it shows that the fine jagged features of the spectra were smoothed out. This reduced noise at the edges of the spectra, but it also risked potential loss of information in the center of the spectra. This can be combatted by windowing spectra components in the NERD software, but one must already know where to window to aid in data retention. Subjective denoising methods, particularly without objective accuracy checks for processed spectra, are susceptible to human bias and over-processing.

A specific challenge limits the effectiveness of the automated thresholding. A central struggle in this project was determining optimal decomposition levels. Srivastava's method relied on an empirical value, which produced high optimal decomposition levels that do not work well with our data, as seen in Figure 9. To tackle this issue, I proposed a different method called the first significant peak method, which, like Srivastava's approach, relied on determining large changes in sparsity. In this method, the optimal decomposition level was the level assigned to where the first significant peak in the sparsity change graph occurred. The rationale was that higher decomposition levels could oversimplify the signal, so the first peak would indicate a high sparsity change while straying away from high decomposition levels.

The first significant peak method appeared to have worked better for specific data types, as seen in Figure 9. Some spectra were given high optimal decomposition levels from Srivastava's optimal level selection code. The definition of a "significant peak" in my method was defined as any peak with an amplitude of at least 10% of the maximum amplitude, which was an arbitrary value. This value was subjectively selected for the data types present in the project. I did not take into consideration other ESR data types. Although the first significant peak method may hold some merit, any observed success may be coincidental. More research is needed to confirm the validity of this method.

This project did not use Srivastava's approach to deriving super-hyperfine and hyperfine components from spectra. This method had a complex chemical background outside this current stage of research. The CWT heat map was promising in this research, as it presented a sea of information where coupling constants can be found, as seen in Figure 13. One route for a continuation of this research is to understand and apply these methods for spectral analysis. However, a method to extract these values, without needing to know them in the first place, was not encountered during this research. The CWT heat map contains prominent patterns of high-intensity pixels, corresponding to wavelet coefficients, which could be key in coupling constant determination.

This project emphasized the capabilities and limitations of wavelet-based denoising for ESR spectroscopy. Although subjective processes and our use of the NERD software were helpful for specific spectra, the lack of objective accuracy checks in this project left room for bias and over-processing. Objective, automated approaches utilizing

Srivastava's methods for decomposition selection and threshold bound determinations showed potential but remain unreliable until a method for finding the optimal decomposition level for all ESR data types is developed. Finally, the CWT heat maps provide an ocean of information for coupling constant determination; however, a defined method for this process does not yet exist and warrants further research. These findings contribute to ESR spectra denoising, coupling constant determination, and a path for future research.

Conclusion

This research explored the applications of wavelet-based denoising methods and coupling constant determination methods of ESR spectra. It compared our subjective use of the NERD software with automated thresholding and denoising. The NERD software was shown to be a helpful tool for denoising spectra; however, our subjective use of the software revealed how easy it is to over-process spectra when spectral features are unknown. An automated approach to denoising, utilizing Srivastava's decomposition selection and threshold bound determination methods, was developed in this project. However, both methods relied on assumptions or empirical values that do not extend to all ESR data types.

This project highlighted the effectiveness of wavelet-based and previous denoising methods. It revealed that effective ESR denoising for all datatypes requires stronger objective approaches to find optimal decomposition levels and accuracy measures to improve noisy spectra clarity and help with data retention. Avenues for future research include developing objective denoising approaches for all data types, the development of a method utilizing CWT heat maps for coupling constant determination, and producing mathematical proofs to validate methods, as well as guarantee accuracy checks and error bounds.

In summary, most of the project goals were met, with coupling constant extraction and optimal decomposition level for all datatypes remaining a primary subject for future research. For specific datasets, denoising was successful; however, some datasets proved unruly for the objective denoising approaches based on Srivastava's work. Accuracy in this research remains unknown until current signal-to-noise ratio calculations are implemented along with potential methods that guarantee accuracy without knowing the actual signal in advance. As one of my math professors, Dr. Domel-White, put it, "It is not safe to do anything." Although this project could not produce a denoising method that guarantees data retention, it was still helpful in contributing to research that may lead to more viable and objective denoising and coupling constant-determining tools in ESR spectroscopy.

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