Table of Contents

[2 Chapter 3 – The Bane of the “Inverse” Problem 1](#_Toc117015555)

[2.1 Lossy information 1](#_Toc117015556)

[2.1.1 Quantum mechanics creates uncertainty 1](#_Toc117015557)

[2.1.2 Transforms lose phase information 1](#_Toc117015558)

[2.2 Workarounds to the “inverse” problem 2](#_Toc117015559)

[2.2.1 Repeat the forward problem 2](#_Toc117015560)

[2.2.2 Bayesian approach 2](#_Toc117015561)

[2.2.3 Linear Combination Fitting (LCF) to references 2](#_Toc117015562)

[2.2.4 Machine Learning 2](#_Toc117015563)

[2.3 References 2](#_Toc117015564)

# Chapter 3 – The Bane of the “Inverse” Problem

In science, an “inverse” problem is using observations to try to calculate the factors that caused them. This is distinct from the forward problem, which starts from causes and then calculates the effects. Inverse problems are often termed “ill-posed”, which means they either (1) don’t have a solution, (2) the solution is not unique, or (3) the solution’s behavior does not change continuously with the initial conditions. In X-ray spectroscopy, the “inverse” problem – going from spectra to structure – often runs into problems with both (2) and (3).

## Lossy information

### Quantum mechanics creates uncertainty

Because of the Heisenberg uncertainty principle, you cannot know exactly both momentum and position, or energy and time. Because excited states have inherent lifetimes, electronic transitions are broadened in energy. Moreover, limits on experiment apparatuses, such as the resolution of your monochromator, have inherent resolution. Thus, any transition too close in energy will be smoothed out and indistinguishable from each other. Other types of spectral broadening can occur from more classical phenomena, such as plasmons and thermal vibrations.

### Transforms lose phase information

In addition to information loss due to quantum mechanics, there is also loss of phase information. This issue is particularly prominent in the interpretation of EXAFS.

### Correlated properties

Another reason why obtaining chemical or geometrical properties directly from spectra is difficult is because of correlated spectra, meaning the two different chemical properties can cause the same spectral feature. Or effects on spectra can be in overlapping energy regions, making it impossible to discern the cause of the feature. [Jahrman, 2022]

## Workarounds to the “inverse” problem

Because there is no proper solution to the “inverse” problem, as there is not a well-defined problem to fix, people have used various work arounds. All these work arounds rely on some amount of prior knowledge of the system. Thus, they turn the inverse problem into an informed inverse problem, making it possible to find a solution.

### Repeat the forward problem

One way to work around the forward problem is to repeatedly perform the forward problem, each time changing the input structure. One can then adjust the input structures depending on the output, which is often theoretically calculated spectra. This process is often how theorists change parameters in their calculations to improve their theoretically calculated spectra and thus match theory and experiment. However, repeating the forward problem is very time intensive, especially when calculation-intensive theories like density functional theory (DFT), or there is a large uncertainty in the possible input structure and thus a large parameter space must be explored.

### Bayesian approach

Another work around is using formal Bayesian statistics to estimate the inverse problem. Although this process has been shown to work, it has not gained any traction in the community because it is very involved; not only is it very inaccessible, but it is computationally and experimentally intensive. Moreover, it also involves formalizing prior knowledge of the system by formalizing a prior in Bayes rule.

cite the Rehr, Kas, Vila papers(s)

### Linear Combination Fitting (LCF) to references

The most common method is linear combination fitting onto reference spectra. This approach assumes that because XAS is an average bulk probe, any components of different structures will contribute directly proportion to their concentration, or percentage of makeup. For example, an experimental sample with 2/3 the iron atoms in a 2+ oxidation state and the other 1/3 of the iron atoms in a 3+ oxidation state will result in a spectrum composed of two parts of an iron 2+ oxidation state reference and one part of an iron 3+ oxidation state reference. Obviously, things can get complicate quickly with the more properties and unknown parameters one must control for. Furthermore, choosing an appropriate library, or reference set, is critical in that it must find a balance between spanning a large enough domain to cover the experimental space but also not have redundant or correlated spectra. This issue becomes especially problematic with the highest uncertainty, or littlest prior knowledge, of the system.

Finally, this method propagates any errors, especially when fitting to theoretical spectra. It can also propagate any systematic errors in the experiment or normalization. It is especially unreliable if all your reference compounds have different second or third coordination shells, which is often the case for solution studies where reference compounds are usually crystalline.

### Machine Learning

Cite Nascimento and Govind, 2022 on TD-DFT providing good enough training data for ML studies

## References