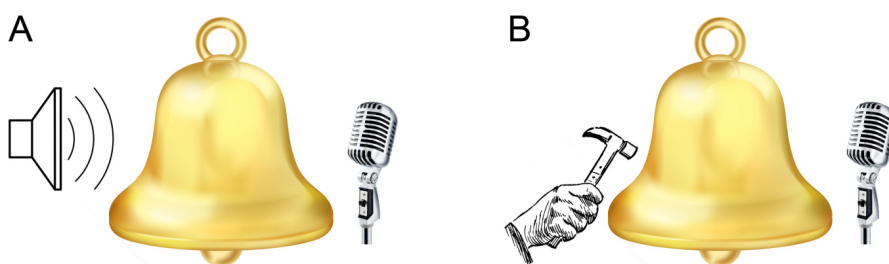


CHEM6154 - Week 20 - Lecture 2 - Fourier spectroscopy

In the old days of electromagnetic spectroscopy, the absorption spectrum of a sample was recorded by measuring energy absorption at each frequency in turn – the so-called *slow passage method*. The arrival of Fourier transform spectroscopy (first in NMR, then ESR, then IR) has brought an improvement in speed and sensitivity. Even though FT methods are often rationalised using physical arguments, the relationship between the pulse and the frequency response of a physical system can be derived from the general mathematical assumptions of linear time-invariant systems theory.

1. Introduction

There are two ways of measuring the resonance frequency spectrum of a bell...



We could use a speaker and a microphone – the speaker would sound every frequency in turn and the microphone would determine which frequencies the bell resonates on (the acoustic power would drop slightly because the bell would absorb it and transform into heat). This would produce the frequency response curve of the bell. Clearly, this is a slow procedure.

Alternatively, we could hit the bell with a hammer and record the sound. It is intuitively clear that the frequencies would be the same; we also know that many other systems behave this way. In this lecture we explore the fundamental reasons for this behaviour as well as their consequences.

2. Linear time-invariant systems

Consider a black box system with an input and an output:

$$\xrightarrow{x(t)} \boxed{\Phi} \xrightarrow{y(t)} \quad \text{OR} \quad y(t) = \Phi\{x(t)\} \quad (1)$$

the system Φ is called *linear time-invariant* (LTI) if:

$$\begin{aligned} \Phi\{\alpha x_1(t) + \beta x_2(t)\} &= \alpha \Phi\{x_1(t)\} + \beta \Phi\{x_2(t)\} = \alpha y_1(t) + \beta y_2(t) \\ \Phi\{x(t - t_0)\} &= y(t - t_0) \end{aligned} \quad (2)$$

where $x(t)$ are input signals, $y(t)$ are output signals and α, β, t_0 are constants. In other words, an LTI system behaves *linearly* with respect to the input signal – a sum of two input signals yields a sum of their corresponding outputs, and multiplying an input by a constant multiplies the output by the same constant. If the input is shifted in time by a constant amount, the system output is shifted by the same amount, but otherwise remains the same – this is called *time invariance*.

3. Pulse response of an LTI system

A hammer strike is a short and sharp input signal – it can be modelled by *Dirac's delta-function* which is a mathematical representation of an infinitely sharp peak with unit area:

$$\delta(t) = \begin{cases} 0 & t \neq 0 \\ \infty & t = 0 \end{cases} \quad \int_{-\infty}^{\infty} \delta(t) dt = 1 \quad (3)$$

The delta-function has the following property:

$$x(t) = \int_{-\infty}^{\infty} x(\tau) \delta(\tau - t) d\tau \quad (4)$$

Let us apply our LTI system to both sides of this expression:

$$\Phi\{x(t)\} = \int_{-\infty}^{\infty} x(\tau) \Phi\{\delta(\tau - t)\} d\tau = \int_{-\infty}^{\infty} x(\tau) h(\tau - t) d\tau \quad (5)$$

The function $h(t) = \Phi\{\delta(t)\}$ is called the *pulse response* of the system. The integral in Equation (5) is called a *convolution*; it is often abbreviated as:

$$\Phi\{x(t)\} = x(t) * h(t) \quad (6)$$

Thus, in some sense, the pulse response $h(t)$ also contains complete information about our linear time-invariant black box Φ and allows us to predict its response to an arbitrary input $x(t)$.

4. Frequency response of an LTI system

To get a physical perspective on the nature of $h(t)$, let us do some continuous-wave spectroscopy on Φ – we supply an oscillating signal (in general, a complex exponential) and see what happens:

$$\Phi\{e^{i\omega t}\} = \int_{-\infty}^{\infty} e^{i\omega\tau} h(\tau - t) d\tau = e^{i\omega t} \int_{-\infty}^{\infty} e^{i\omega(\tau - t)} h(\tau - t) d\tau = e^{i\omega t} \int_{-\infty}^{\infty} h(\tau) e^{i\omega\tau} d\tau = H(\omega) e^{i\omega t} \quad (7)$$

where $H(\omega)$ gives the value of the integral, which depends on the frequency parameter ω . This demonstrates that *exponentials are eigenfunctions of LTI systems*. That is, an LTI system cannot shift frequencies, it can only alter their coefficients.

The function $H(\omega)$ is called the *frequency response* of the system. It is the analogue of the slow-passage electromagnetic spectrum. We now use the convolution definition from Equation (5):

$$\Phi\{e^{i\omega t}\} = \int_{-\infty}^{\infty} e^{i\omega\tau} h(\tau - t) d\tau = \int_{-\infty}^{\infty} e^{i\omega(t + \tau)} h(\tau) d\tau = \left(\int_{-\infty}^{\infty} h(\tau) e^{i\omega\tau} d\tau \right) e^{i\omega t} \quad (8)$$

After comparing this with Equation (7), we arrive at our final result:

$$H(\omega) = \int_{-\infty}^{\infty} h(\tau) e^{i\omega\tau} d\tau \quad (9)$$

In other words, *the frequency response ("spectrum") of a linear time-invariant system is a Fourier transform of its pulse response ("free induction decay")*. Equation (9) highlights the central role of the Fourier transform in electromagnetic spectroscopy. There is nothing special about bells and NMR – all LTI sys-

tems behave like that. It should be noted that LTI is an approximation – most real systems are not perfectly linear and real pulses are never perfectly sharp.

5. Sampling and preprocessing of oscillatory signals

Before we start with the formal theory of spin systems, it would be wise to get our datasets into the best shape possible. This section gives a brief overview.

5.1 Sampling rate and Nyquist condition

Sampling rate is the number of points per unit time used to represent a time domain signal in a discrete form. The minimum sampling rate is dictated by the highest frequency present in the signal.

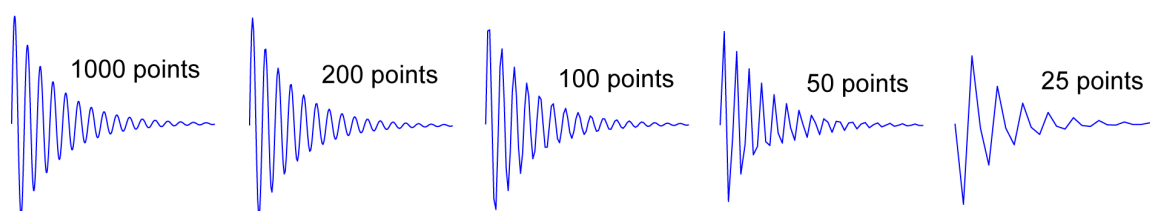


Figure 1. A decaying oscillation digitized at different sampling rates. Note the frequency distortion in the rightmost trace.

Nyquist condition: perfect reconstruction of a time domain signal from digital samples is possible if and only if the sampling rate exceeds two points per period of the fastest oscillation found in the signal.

In NMR, the consequences of **undersampling** a free induction decay are severe – high-frequency signals end up in the wrong place. This phenomenon is called **aliasing** (Figure 2).

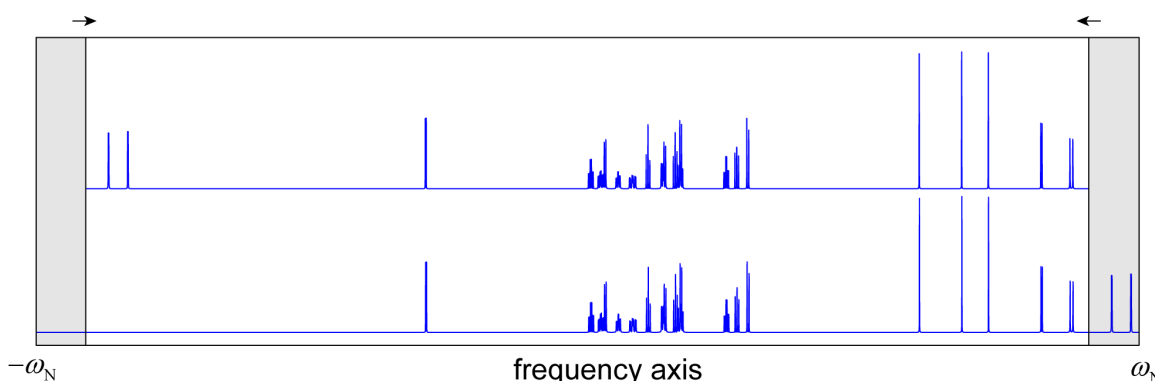


Figure 2. Frequency distortion caused by sub-Nyquist sampling. Note the two methyl peaks folding over the spectrum edge.

For a true frequency f sampled at a frequency f_s , the apparent frequency as a result of aliasing is:

$$f_{\text{app}} = f - nf_s, \quad n = \left\lfloor \frac{f + f_s/2}{f_s} \right\rfloor \quad (10)$$

where the brackets indicate rounding down.

5.2 Digital resolution and zerofilling

Digital resolution is the number of points per unit frequency used to represent a frequency domain signal in a discrete form.

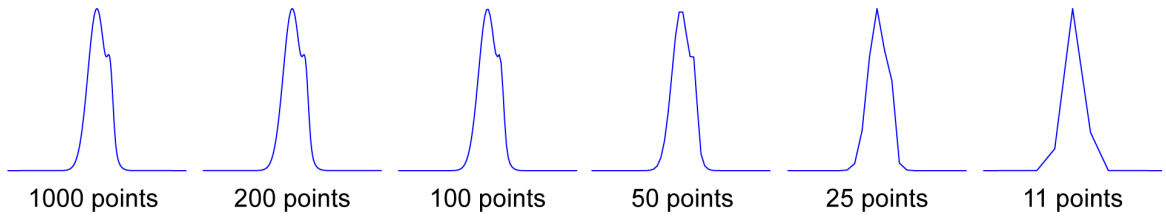


Figure 3. A pair of overlapping peaks digitized with different resolution. Note the gradual loss of detail from left to right.

The accuracy of quantification (peak picking, integration, etc.) is influenced by the digital resolution. One way of improving it is to pad the time-domain signal with zeros. We will skip the formal proof here, but this **zerofilling** procedure in the time domain is equivalent to interpolation in the frequency domain: the frequency sampling step becomes finer (Figure 4).

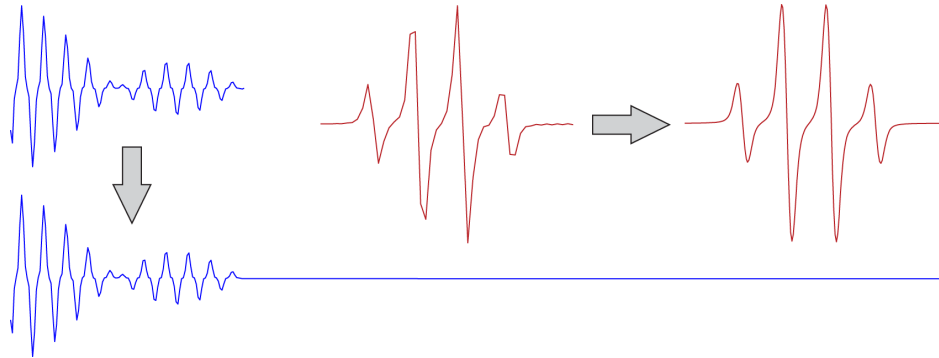


Figure 4. Improvement in digital resolution of an ESR signal resulting from time-domain zerofilling.

Sharp magnetic resonance signals often require zerofilling to be integrated accurately (Figure 4).

5.3 Convolution filters and window functions

Consider a local averaging filter in Figure 5. Such filters are useful in NMR spectroscopy because they improve the signal-to-noise ratio by removing high-frequency noise.

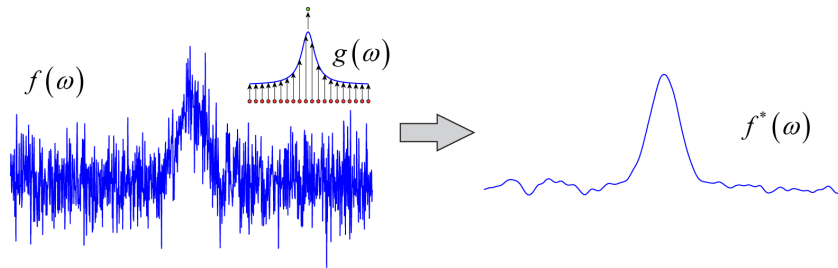


Figure 5. The result of the application of a Lorentzian local averaging filter to a noisy peak.

Mathematically speaking, this is a convolution of the spectrum $f(\omega)$ with some bell-shaped curve $g(\omega)$, for example a Lorentzian function $g(\omega) = 1/(1 + \omega^2)$:

$$f^*(\omega) \leftarrow \int_{-\infty}^{\infty} f(\nu) g(\omega - \nu) d\nu \quad (11)$$

The inverse Fourier transform of a Lorentzian function is an exponential function:

$$\int_{-\infty}^{\infty} \frac{1}{1 + \omega^2} e^{i\omega x} d\omega = e^{-|x|} \quad (12)$$

Therefore, by the same mathematics as in Section 3, the application of a Lorentzian smoothing *convolution filter* in the frequency domain is equivalent to forcing a decay in the time domain. Such decaying functions (an exponential in this case) are called *window functions*.