

5.4: Fourier Transformation (FT)- from an FID to a Spectrum

This Chapter introduces the most generally applied method for conversion of raw NMR signal (FID) to NMR spectra- Fourier transformation (FT). Specifically, we will see how the key parameters of an FID introduced in the previous chapter (S_0 , R and Ω) affect the key properties of an NMR spectral resonance: position, intensity and linewidth. We will also demonstrate how Fourier transformation applied to a combined FID generated by multiple spin- $\frac{1}{2}$ nuclei leads to a spectrum with multiple respective resonance lines, that is we will demonstrate mathematical linearity of FT.

Learning Objectives

- Introduce the basic mathematical description of Fourier transformation (FT)
- Grasp how FT converts time-domain function into a frequency-domain function
- Learn how FT operates: it samples frequency values for the best matches to the oscillating FID
- Appreciate how FT deconvolutes an FID from multiple nuclei into respective NMR spectral lines or from FIDs of differing intensities.
- Determine how key FID parameters (S_0 , R , Ω) affect the position, intensity and linewidth of the corresponding NMR spectral line via FT.

Fourier transformation as method to produce an NMR spectral line from FID

Historically, the very first NMR spectra for spin- $\frac{1}{2}$ nuclei were collected very inefficiently: one frequency was sampled at a time by subjecting a target system at thermal equilibrium to an excitation (B1 field) alternating at a specific frequency value. This was very slow: after each excitation the system needed time to relax back to thermal equilibrium. Worse yet, such a slow pace of recording did not allow for repetition of the data collection thus the sensitivity of the recordings was low and the resolution – very limited (more on sensitivity and resolution of NMR later). In order to bypass this bottleneck, Swiss scientist Richard Ernst applied a well-known method – Fourier transformation for processing of raw NMR data – FID or $S(t)$ signal vs. time t . This allowed a much faster approach: the system is excited by a broad range of frequencies at once and the response is deconvoluted via digital Fourier transformation (FT). The resulting acceleration of recordings and gains in sensitivity/resolution were so dramatic that it immediately made NMR a central method: practical, wide-spread and rapidly developing into various applications. For this contribution, Richard Ernst was awarded a Nobel prize in Chemistry in 1991 for the “development of the method of high-resolution nuclear magnetic resonance (NMR) spectroscopy”. Figure V.4.A and Equation V.4.1 introduce Fourier transformation and its application for converting an FID into a spectral line.

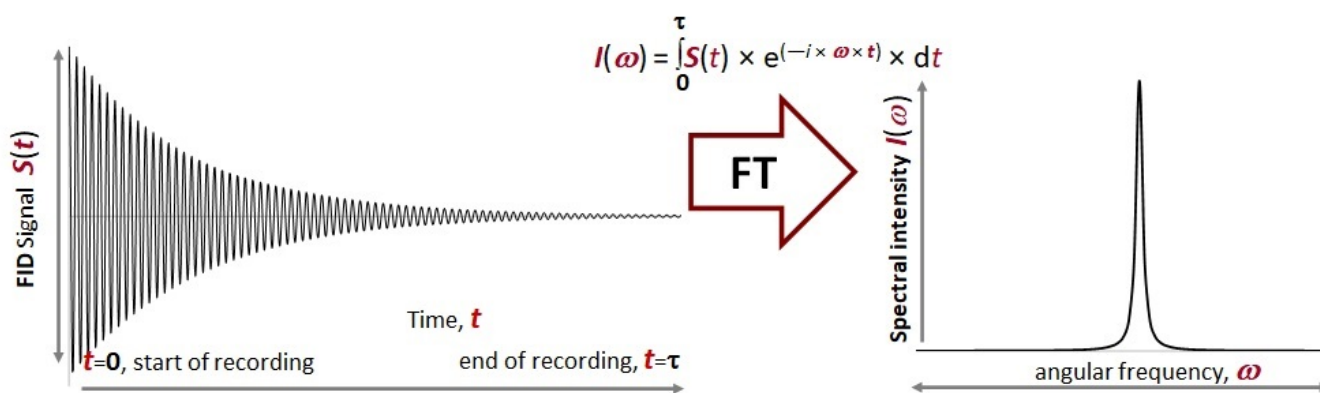


Figure V.4.A The most general way to produce an NMR spectral line from the raw FID recorded signal via Fourier transformation (FT). See Examples and Practice problems below for the actual application of FT for the FID approximation introduced in this text. For $S(t)$ shown here, a single angular frequency oscillation was chosen.

Mathematically, Fourier transformation is equivalent to trying to find the “best harmonic sin/cos match $I(\omega)$ to the target oscillating function” by applying the following treatment to the target function of time $S(t)$:

Equation 5.4.1

$$I(\omega) = \int_0^{\tau} S(t) \cdot e^{-i \cdot \omega \cdot t} dt \quad (5.4.1)$$

Note

Mathematically, $e^{i \cdot x}$ or “complex exponent represents the following expression: $e^{i \cdot x} = \cos(x) + i \cdot \sin(x)$ where i is called the “complex iota”, which is defined as $i^2 = -1$. In this equation, $\cos(x)$ is called the “real part” and $\sin(x)$ is called the “imaginary part” of the complex exponent. Complex exponent is a way to treat a trigonometric sin/cos combination (needed for the correct phase determination) via a much cleaner and simpler “exponential math”.

From **Equation V.4.1** above, we can appreciate that FT operates by trying multiplication of the target function by a $\cos(\omega t)$ for every angular frequency ω with the goal of detecting the specific ω value giving the maximum value for the integration. The maximum value $I(\omega)$ will be thus obtained at $\omega = \Omega$, the resonance angular frequency of the target spin- $\frac{1}{2}$ nucleus. Note that because FT is based on an integration (a linear mathematical operation), an FID composed of signals from multiple sources oscillating at multiple resonance frequencies, the produced spectrum $I(\omega)$ will have multiple “peaks”, corresponding to those multiple frequencies of oscillations (see Examples below).

✓ Example 5.4.1

On mathematical linearity of FT. Starting from Equation V.4.1 and Figure V.4.A above, show that the FID signal originating from a s system of two spin- $\frac{1}{2}$ protons will be converted via FT into a spectrum containing two peaks such that the resulting spectrum is a sum of the two individual spectra as if each of them were recorded and processed separately.

Solution

To prove the requested, first, let’s describe mathematically the combined FID from two sources, $S(t) = S_1(t) + S_2(t)$. Therefore:

Equation 5.4.4

$$I(\omega) = \int_0^\tau (S_1(t) + S_2(t)) \cdot e^{-i \cdot \omega \cdot t} dt \quad (5.4.2)$$

$$I(\omega) = \int_0^\tau S_1(t) \cdot e^{-i \cdot \omega \cdot t} dt + \int_0^\tau S_2(t) \cdot e^{-i \cdot \omega \cdot t} dt \quad (5.4.3)$$

$$I(\omega) = I_1(\omega) + I_2(\omega) \quad (5.4.4)$$

Thus we demonstrated that because of the mathematical linearity of the integration (and FT), the spectra resulting from FT-processed FIDs are additive as well.

✓ Example 5.4.2

Parameter S_0 in **Equation V.3.2** describing how the FID signal depends on time (Chapter V.3) corresponds to the initial signal (electric current detected at time $t=0$). Demonstrate that the spectrum resulting from FT processing of the FID grows linearly with S_0 : that is if S_0 doubles, the spectral intensity will double as well.

Solution

To prove the requested, we will plug $S(t)$ as described in **Equation V.3.2** into Fourier transformation in **Equation V.4.1** and check how the result of the integration depends on S_0 :

Equation 5.4.7

$$I(\omega) = \int_0^\tau S(t) \cdot e^{-i \cdot \omega \cdot t} dt \quad (5.4.5)$$

$$I(\omega) = \int_0^\tau S_0 \cdot e^{-R \cdot t} \cdot e^{i \cdot \Omega \cdot t} \cdot e^{-i \cdot \omega \cdot t} dt \quad (5.4.6)$$

$$I(\omega) = S_0 \cdot \int_0^\tau e^{-R \cdot t} \cdot e^{i \cdot \Omega \cdot t} \cdot e^{-i \cdot \omega \cdot t} dt \quad (5.4.7)$$

The last formula above shows that $I(\omega)$ depends linearly on S_0 since S_0 is simply a multiplication factor for the rest of the expression.

Key Result: Examples 1 and 2 above show that Fourier transformation is a mathematically linear treatment. Specifically, FID composed of a sum of signals from multiple nuclei will be FT-processed into a spectrum, which is a sum of individual spectra originating from the respective nuclei. Likewise, scaling the initial signal intensity (and thus the entire FID) up or down will result in proportionately scaled up or down of the spectrum produced from this FID via FT.

This key property of Fourier transformation as well as that fact that it is very amenable for digital treatment (this is with computer software) explains why this method of producing NMR spectra from raw NMR data (FIDs) is the most widely used today although a number of respectable alternatives to FT do exist.

Practice Problems

Problem 1. Using Excel, Origin or any other suitable spreadsheet software, build a simple FID or $S(t)$ function according to the following formula:

$S(t) = S_0 \cdot e^{-R \cdot t} \cdot \cos(\Omega \cdot t)$ where time t is the independent variable, $S(t)$ is the function of t , whereas S_0 , R and Ω are parameters (constants). Specify S_0 , R and Ω values in their respective data cells. Using this function, build a plot S vs. t and explore how its shape changes in response to your alteration of each of the three parameters (vary them one-by-one).

Problem 2. Starting from Equation 5.4.7 above, transform the FT for $S(t)$ in such a way that under the exponent there is a single exponential function only (not a product of three exponents). Is this single-exponent integral easy to “take” to determine $I(\omega)$?

Problem 3*. Starting from the result for Problem 2 above, determine the $I(\omega)$ under the assumption of the sufficiently long acquisition time $\tau \gg 1/R$. This condition effectively states that NMR data recording will start at certain time $t=0$ and continue until $t=\tau$, where τ is much larger than the characteristic relaxation time $1/R$. To determine $I(\omega)$, only the “real part” of the complex integration result is needed (the “complex part” can be ignored). Also, the following complex math hint can be useful:

$$\frac{1}{a+i \cdot b} = \frac{(a-i \cdot b)}{(a-i \cdot b) \cdot (a+i \cdot b)} = \frac{a}{a^2+b^2} - i \cdot \frac{b}{a^2+b^2}$$

Problem 4*. Each NMR spectrum is reporting signals only within a certain range of frequencies (SW: spectral width). With the idea of a “digital FID”, a finite set of of current vs. time $S(t)$ data points, processed with Fourier transformation and reporting frequencies ω within a certain range ($\omega_{\min} < \omega < \omega_{\max}$; $\omega_{\max} - \omega_{\min} = \text{SW}$, spectral width), predict how a resonance with a frequency outside of this range ($\omega < \omega_{\min}$ or $\omega > \omega_{\max}$) would be represented on the digital NMR spectrum?

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