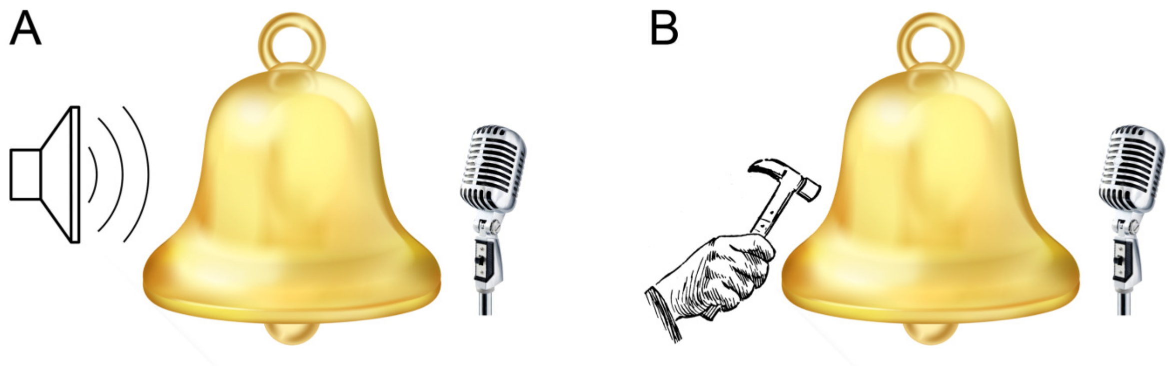
Module I, Lecture 1: Introduction to Fourier Spectroscopy

In the old days of electromagnetic spectroscopy, the absorption spectrum of the 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 caused a major improvement in speed and sensitivity. Even though the FT methods are often rationalized using physical arguments, the exact relationship between the pulse and the frequency response of a physical system can be derived from general mathematical assumptions used in the LTI (linear time-invariant) systems theory.

Introduction

There are two ways of measuring the 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 very slow procedure.

Alternatively, we could hit the bell with a hammer and record the sound it produces. It is intuitively clear that the frequencies we hear would be the same, and we have heard in our spectroscopy course that the ring-back and the frequency response are related by a Fourier transform. We also know that many other physical systems behave in the same way. In this lecture we will explore the fundamental reasons for this behaviour as well as their consequences.

Linear time-invariant systems

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

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

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

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

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 returns a sum of their corresponding outputs and multiplying an input by a constant number multiplies the output by the same number. 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*.

The input function $x(t)$ can be expanded in some orthonormal discrete basis set $\{g_k(t)\}$ (any complete basis would work, the practical choice depends on the nature of the system and convenience):

$$x(t)=\sum_k \chi_k g_k(t), \qquad \chi_k = \langle g_k(t)|x(t)\rangle = \int_{-\infty}^{\infty} g_k^*(t)x(t)\,dt, \qquad k=0,1,2... \tag{3}$$

where the star denotes complex conjugation. In the continuous limit, the input function may be given in terms of an integral transform with some user-specified kernel $g(\tau,t)$:

$$x(t)=\int_{-\infty}^{\infty}\chi(\tau)g(\tau,t)\,d\tau \tag{4}$$

The response to an arbitrary input function can then be written in terms of responses to either the individual basis functions or the integral transform kernel:

$$\Phi\{x(t)\}=\sum_k \chi_k \Phi\{g_k(t)\}=\int_{-\infty}^{\infty}\chi(\tau)\Phi\{g(\tau,t)\}\,d\tau \tag{5}$$

This means that the set of responses to the basis functions defines an LTI system completely – a known library of responses to $\{g_k(t)\}$ would allow us to predict the response to any input.

Pulse response

A hammer strike amounts to a very short and sharp input signal – a delta-function. One of its basic properties (see your functional analysis course) is:

$$f(x_0)=\int_{-\infty}^{\infty}f(x)\delta(x-x_0)\,dx \quad\Rightarrow\quad x(t)=\int_{-\infty}^{\infty}x(\tau)\delta(\tau-t)\,d\tau \tag{6}$$

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

$$\Phi\{x(t)\}=\int_{-\infty}^{\infty}x(\tau)\Phi\{\delta(\tau-t)\}\,dx=\int_{-\infty}^{\infty}x(\tau)h(\tau-t)\,d\tau \tag{7}$$

The function $h(t)=\Phi\{\delta(t)\}$ is called the *pulse response* of the system. The integral in Equation (7) is known as the *convolution integral*, and is often abbreviated as:

$$\Phi\{x(t)\}=x(t)*h(t) \tag{8}$$

So, 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 $x(t)$.

Frequency response

To get a physical perspective on the nature of $h(t)$, let us do some continuous-wave spectroscopy on Φ and feed an oscillating signal (in general, a complex exponential) into it. We then have:

$$\Phi\left\{e^{\mathrm{i}\omega t}\right\}=\int_{-\infty}^{\infty} e^{\mathrm{i}\omega\tau}h(\tau-t)\,d\tau=e^{\mathrm{i}\omega t}\int_{-\infty}^{\infty} e^{\mathrm{i}\omega(\tau-t)}h(\tau-t)\,d\tau=e^{\mathrm{i}\omega t}\int_{-\infty}^{\infty} h(\tau)e^{\mathrm{i}\omega\tau}\,d\tau=H(\omega)e^{\mathrm{i}\omega t} \tag{9}$$

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. It is defined by Equation (9), but we can also use the convolution definition from Equation (7):

$$\Phi\left\{e^{\mathrm{i}\omega t}\right\}=\int_{-\infty}^{\infty} e^{\mathrm{i}\omega\tau}h(\tau-t)\,d\tau=\int_{-\infty}^{\infty} e^{\mathrm{i}\omega(t+\tau)}h(\tau)\,d\tau=\left(\int_{-\infty}^{\infty} h(\tau)e^{\mathrm{i}\omega\tau}\,d\tau\right)e^{\mathrm{i}\omega t} \tag{10}$$

After comparing this with Equation (9), we arrive at our final result:

$$H(\omega)=\int_{-\infty}^{\infty} h(\tau)e^{\mathrm{i}\omega\tau}\,d\tau \tag{11}$$

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 (11) highlights the central role of the Fourier transform in electromagnetic spectroscopy. There is nothing special about bells and NMR – all LTI systems 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.

Properties of the Fourier transform

The overall multipliers in the definition may vary from one book to another, the definition below is chosen to yield a unitary transformation (the 2-norm of the function is preserved):

$$F_{+}\left\{f(t)\right\}=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(t)e^{-\mathrm{i}\omega t}\,dt \qquad F_{-}\left\{f(t)\right\}=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(t)e^{\mathrm{i}\omega t}\,dt \tag{12}$$

The two transforms are exact mirrors of one another, labelling one "forward" and the other "backward" is a matter of choosing the convention for the frequency signs. In the subsequent property proofs we will assume that the functions are sufficiently well-behaved for the various transformations to hold.

1. Forward and backward Fourier transforms are each other's inverse. This can be proven by direct inspection and we would have to make use of one of the definitions of delta function, namely:

$$\delta(t)=\frac{1}{2\pi}P\int_{-\infty}^{\infty} e^{\mathrm{i}\omega t}\,d\omega \tag{13}$$

Where P indicates Cauchy principal value. With that in place, we have:

$$\begin{aligned}F_{+}\left\{F_{-}\left\{f(t)\right\}\right\}&=\frac{1}{2\pi}\int_{-\infty}^{\infty}\left[\int_{-\infty}^{\infty} f(t')e^{\mathrm{i}\omega t'}\,dt'\right]e^{-\mathrm{i}\omega t}\,d\omega=\frac{1}{2\pi}\int_{-\infty}^{\infty} f(t')\,dt'\int_{-\infty}^{\infty} e^{\mathrm{i}\omega(t'-t)}\,d\omega=\\&=\int_{-\infty}^{\infty} f(t')\delta(t'-t)\,dt'=f(t),\qquad F_{-}\left\{F_{+}\left\{f(t)\right\}\right\}=\ldots=f(t)\end{aligned} \tag{14}$$

Note that most software packages place the zero frequency on the *edge* of the spectrum – look out for commands like Matlab's `fftshift` if your spectrum does not look the way you expect it to.

2. Fourier transform is linear. For any two functions $f(t)$, $g(t)$ and for any two scalars α, β:

$$F_{\pm}\left\{\alpha f(t)+\beta g(t)\right\}=\alpha F_{\pm}\left\{f(t)\right\}+\beta F_{\pm}\left\{g(t)\right\} \tag{15}$$

The proof is obvious and relies on the linearity of the integration operation in Equations (12).

3. Fourier transform of a derivative is related to the Fourier transform of the original function. To prove this property in full generality we need to start with the k-th derivative of a function $f(t)$ and carry out one stage of integration by parts:

$$\begin{gathered}F_{\pm}\left\{f^{(k)}(t)\right\}=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}f^{(k)}(t)e^{\mp i\omega t}dt=\left\{\begin{matrix}u=e^{\mp i\omega t} & du=\mp i\omega e^{\mp i\omega t}dt\\ dv=f^{(k)}(t)dt & v=f^{(k-1)}(t)\end{matrix}\right\}=\\ =e^{\mp i\omega t}f^{(k-1)}(t)\Big|_{-\infty}^{\infty}+\frac{\pm i\omega}{\sqrt{2\pi}}\int_{-\infty}^{\infty}f^{(k-1)}(t)e^{\mp i\omega t}dt=\frac{\pm i\omega}{\sqrt{2\pi}}\int_{-\infty}^{\infty}f^{(k-1)}(t)e^{\mp i\omega t}dt=(\pm i\omega)F_{\pm}\left\{f^{(k-1)}(t)\right\}\end{gathered} \tag{16}$$

We can see that the order of the derivative has been reduced by one and the $\pm i\omega$ multiplier popped out in front. Repeating this process multiple times, we eventually get:

$$F_{\pm}\left\{f^{(k)}(t)\right\}=(\pm i\omega)^{k}F_{\pm}\left\{f(t)\right\} \tag{17}$$

This property is useful for solving differential equations because it transforms them into algebraic equations that are easier to solve.

4. Derivative of a Fourier transform is related to the Fourier transform of the original function. Writing the k-th derivative with respect to the variable ω of the Fourier transform, we get:

$$\begin{gathered}\left[F_{\pm}\left\{f(t)\right\}\right]^{(k)}=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\left[f(t)e^{\mp i\omega t}\right]^{(k)}dt=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}f(t)\left[e^{\mp i\omega t}\right]^{(k)}dt=\\ =\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}(\mp it)^{k}f(t)e^{\mp i\omega t}dt=(\mp i)^{k}F_{\pm}\left\{t^{k}f(t)\right\}\end{gathered} \tag{18}$$

In which a derivative of $e^{\mp i\omega t}$ with respect to ω has simply been taken k times and the result simplified. Equations (17) and (18) are useful for solving ODEs and PDEs – a differential equation in the time domain is transformed into an algebraic equation in the frequency domain.

5. Convolution in the time domain is equivalent to multiplication in the frequency domain and convolution in the frequency domain is equivalent to multiplication in the time domain:

$$f*g=\int_{-\infty}^{\infty}f(\tau)g(t-\tau)d\tau=F_{-}\left\{F_{+}\left\{f(t)\right\}F_{+}\left\{g(t)\right\}\right\}=F_{+}\left\{F_{-}\left\{f(t)\right\}F_{-}\left\{g(t)\right\}\right\} \tag{19}$$

This is known as the *convolution theorem*. It may be proven by a somewhat lengthy direct inspection process. Writing out the Fourier transforms and simplifying yields:

$$F_{-}\left\{F_{+}\left\{f(t)\right\}F_{+}\left\{g(t)\right\}\right\}=\frac{1}{2\pi}\int_{-\infty}^{\infty}\left[\int_{-\infty}^{\infty}f(t')e^{-i\omega t'}dt'\right]\left[\int_{-\infty}^{\infty}g(t'')e^{-i\omega t''}dt''\right]e^{i\omega t}d\omega \tag{20}$$

where a pair of Fourier transforms was used with a coefficient of 1 in front of the forward one and a coefficient of $(2\pi)^{-1}$ in front of the backward one. Absorbing the $e^{i\omega t}$ term under the integral in the first set of brackets produces:

$$F_{-}\left\{F_{+}\left\{f(t)\right\}F_{+}\left\{g(t)\right\}\right\}=\frac{1}{2\pi}\int_{-\infty}^{\infty}\left[\int_{-\infty}^{\infty}f(t')e^{-i\omega(t'-t)}dt'\right]\left[\int_{-\infty}^{\infty}g(t'')e^{-i\omega t''}dt''\right]d\omega \tag{21}$$

Shifting the integration variable under the first set of brackets yields:

$$F_{-}\left\{F_{+}\left\{f(t)\right\}F_{+}\left\{g(t)\right\}\right\}=\frac{1}{2\pi}\int_{-\infty}^{\infty}\left[\int_{-\infty}^{\infty}f(t'+t)e^{-i\omega t'}dt'\right]\left[\int_{-\infty}^{\infty}g(t'')e^{-i\omega t''}dt''\right]d\omega \tag{22}$$

Rearranging the integrals to take the ω integral first then yields:

$$F_{-}\left\{F_{+}\left\{f(t)\right\}F_{+}\left\{g(t)\right\}\right\}=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt'\int_{-\infty}^{\infty}dt''\left[f(t'+t)g(t'')\int_{-\infty}^{\infty}e^{-i\omega(t'+t'')}d\omega\right] \tag{23}$$

After we recognize the delta function and use the property given in Equation (6), we get:

$$\begin{aligned}F_{-}\left\{F_{+}\left\{f(t)\right\}F_{+}\left\{g(t)\right\}\right\}&=\int_{-\infty}^{\infty}dt'\int_{-\infty}^{\infty}dt''f(t'+t)g(t'')\delta(t'+t'')=\\&=\int_{-\infty}^{\infty}f(t-t'')g(t'')dt''=f*g\end{aligned} \tag{24}$$

The $F_{+}\left\{F_{-}\left\{f(t)\right\}F_{-}\left\{g(t)\right\}\right\}$ case is proven in a similar fashion. An alternative formulation of the convolution theorem is:

$$F_{\pm}\left\{f*g\right\}=F_{\pm}\left\{f(t)\right\}F_{\pm}\left\{g(t)\right\} \tag{25}$$

Just as above, care needs to be taken about the multipliers in front of the forward and backward transformations. A corollary of the convolution theorem, called *Wiener-Khinchin theorem*, provides a simple way to evaluate autocorrelation functions:

$$\int_{-\infty}^{\infty}f^{*}(\tau)f(t+\tau)d\tau=F_{+}\left\{\left|F_{-}\left\{f(t)\right\}\right|^{2}\right\} \tag{26}$$

Equation (25) will be useful when we deal with window functions and Equation (26) will come up during the calculation of correlation functions in spin relaxation theory.

6. When time is shifted in the input function, the Fourier transform is modulated:

$$F_{\pm}\left\{f(t-t_0)\right\}=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}f(t-t_0)e^{\mp\mathrm{i}\omega t}dt=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}f(t)e^{\mp\mathrm{i}\omega(t+t_0)}dt=e^{\mp\mathrm{i}\omega t_0}F_{\pm}\left\{f(t)\right\} \tag{27}$$

Reciprocally, the Fourier transform of a modulated function ends up being shifted:

$$F_{\pm}\left\{e^{\mathrm{i}\omega_0 t}f(t)\right\}=\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}f(t)e^{\mp\mathrm{i}(\omega\mp\omega_0)t}=F_{\pm}\left\{f(t)\right\}(\omega\mp\omega_0) \tag{28}$$

These relations constitute the *modulation theorem* for the Fourier transforms.

7. Fourier transform is a unitary operator, assuming the coefficients used are as given in Equation (12). This may also be proven by direct inspection. For the forward transform:

$$\begin{aligned}
&\int_{-\infty}^{\infty}\left|F_{+}\{f(t)\}\right|^{2}d\omega=\int_{-\infty}^{\infty}\left[\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}f(t)e^{-i\omega t}dt\right]\left[\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}f^{*}(t')e^{i\omega t'}dt'\right]d\omega=\\
&=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\int_{-\infty}^{\infty}dt'\left[f(t)f^{*}(t')\int_{-\infty}^{\infty}e^{-i\omega(t-t')}d\omega\right]=\int_{-\infty}^{\infty}dt\int_{-\infty}^{\infty}dt'\left[f(t)f^{*}(t')\delta(t'-t)\right]=\\
&=\int_{-\infty}^{\infty}f(t)f^{*}(t)dt=\int_{-\infty}^{\infty}\left|f(t)\right|^{2}dt
\end{aligned}\tag{29}$$

Because the integral below is related to the total signal power, this is known as the *power theorem*.

Discrete and 'fast' Fourier transform

For discrete data, the integral in Equations (12) is replaced by the corresponding Riemann sum:

$$\left[F_{\pm}\{f\}\right]_{n}=\frac{1}{N\sqrt{2\pi}}\sum_{k=0}^{N-1}f_{k}e^{\mp\frac{ikn}{N}}\tag{30}$$

where N is the total number of digitization points in the signal, and the points are assumed to be uniformly spaced. The sum in Equation (30) has to be computed for every point in the spectrum, meaning that $O(N^2)$ multiplications are required for a size N Fourier transform. This makes brute-force evaluation slow. For the special case of $N=2^n$, where n is a small integer, the Fourier transform can be broken down into smaller chunks, yielding $O(N\log_2 N)$ scaling, which is much better. This is known as *fast Fourier transform*, and it is the one used in most software packages these days.

Further reading

1. Ernst, R.R., Anderson, W.A., *Application of Fourier transform spectroscopy to magnetic resonance*, Review of Scientific Instruments, 1966, 37, 93-102.
2. Derome, A.E., *Modern NMR techniques for chemistry research*, Pergamon, 1987 – Chapter 2.
3. Ernst, R.R., Bodenhausen, G., Wokaun, A., *Principles of nuclear magnetic resonance in one and two dimensions*, Oxford University Press, 2004 – Section 4.1.