8.1. The Fourier transform

The Fourier transform is an essential tool of pulsed NMR spectroscopy. In essence, the Fourier transform extracts the amplitudes and frequencies of the NMR resonances from the free induction decay (FID). The Fourier transform can be described in terms of vector algebra and geometry. As a grossly simple example, assume that there are three frequencies (v_1,v_2,v_3) in an FID with amplitudes (a,b,c). The FID can be represented as a three dimensional vector having components along three orthogonal frequency axes v_1, v_2, and v_3 with amplitudes a, b, and c. The amplitude of each frequency can be obtained by projecting (by the dot product) the FID vector onto the three orthogonal axes.

The Fourier transform projects the FID "vector" on to a set of orthogonal axes of frequencies. The axes of the Fourier transform are the orthogonal set of sine and cosine functions of different frequencies. In the integral Fourier transform there are an infinite number of "axes" and the frequency resolution is continuous. For a real spectrum where the frequency range is represented by a finite number of data points, say 8192, each data point represents a different frequency "axis" in a space with 8192 orthogonal dimensions. A space of this dimension is somewhat difficult to visualize without the assistance of forbidden substances, but if the amplitudes of these frequency vectors are plotted as a 8192 column histogram, which represent all of the the orthogonal axes, the result is an amplitude versus frequency plot identical to the familiar one-dimensional NMR spectrum. Each data point along the frequency dimension represents an orthogonal axis and the amplitude at that frequency is the projection of the FID vector onto that axis.

8.2. Free Induction Decay

The free induction decay (FID) is represented as a sum of exponentially decaying, oscillating functions,

$$F(t) = \sum_{0}^{t} e^{i\pi v_i t} \, e^{-t/T_2} \qquad \textbf{(1)}$$

The exponential function with the imaginary argument implies that the signal was collected simultaneously along two orthogonal axes, X and Y. The $2\pi v_i$ are the detected audio frequencies (in Hertz) of the NMR resonances. The exponential decay constant (T_2) is related to the line width of the peak at half height.

$$\Delta v_{1/2} = 1/(\pi T_2) \qquad \textbf{(2)}$$

Every peak in the spectrum gives rise to an FID. Manual extraction of a frequency from an FID is simple if there is only one resonance line, the reciprocal of the *period* or the time for one cycle is the frequency. In an FID that consists of the sum of more than one resonance line, a manual analysis is not as easy since all of the signals are summed together. The Fourier transform is one way to extract the information, there are other methods such as linear prediction, Baysian analysis, and maximum entropy which will not be discussed.

8.3. The Fourier Transform

The Fourier transform is defined as:

$$S(\mathrm{v}) = \int_0^\infty F(t)\, e^{-i2\pi \mathrm{v}_0 t} dt \qquad \textbf{(1)}$$

and substituting the FID for F(t) we obtain,

$$S(\mathrm{v}) = \int_0^\infty e^{i2\pi \mathrm{v}_i t}\, e^{-t/T_2}\, e^{i2\pi \mathrm{v}_0 t} \qquad \textbf{(2)}$$

The solution of this integral (Eqn. 1.3.2) is as follows:

$$S(\mathrm{v}) = \int_0^\infty e^{-\,(i2\pi(\mathrm{v}_0 - \mathrm{v}_i) \,+\, 1/T_2)t}\; dt \qquad \textbf{(3)}$$

The integral of exponential functions is especially easy to remember,

$$\int_0^\infty e^{At} dt = \frac{1}{A} e^{At}\Big]_0^\infty \qquad \textbf{(4)}$$

and thus we can solve the integral in Equation 1.3.3.

$$S(\nu) = \frac{-1}{i2\pi\Delta\nu + 1/T_2} * e^{-i(2\pi(\nu_i - \nu_0) - 1/T_2)t}\Big]_0^{\infty} \quad \textbf{(5)}$$

evaluating the limits with the facts that $e^{-\infty} = 0$ and $e^0 = 1$, and further separating the real and imaginary parts we obtain,

$$\begin{aligned} S(\nu) &= \frac{1}{i2\pi\Delta\nu + 1/T_2} \\ &= \frac{T_2}{1 + i2\pi\Delta\nu T_2} \\ &= \frac{T_2}{1 + i2\pi\Delta\nu T_2} * \frac{1 - i2\pi\Delta\nu T_2}{1 - i2\pi\Delta\nu T_2} \\ &= \underbrace{\frac{T_2}{1 + (2\pi\Delta\nu T_2)^2}}_{\textit{Absorption}} - i * \underbrace{\frac{2\pi\Delta\nu T_2^2}{1 + (2\pi\Delta\nu T_2)^2}}_{\textit{Dispersion}} \end{aligned} \quad \textbf{(6)}$$

The two line shapes were discussed in Chapter 1.

8.4. Fourier Transform of Real Data

If the NMR signal is detected along a single axis, then the data collected are amplitude modulated (real) and the relative phase of the signal with respect to the carrier frequency is unknown, i.e., one cannot determine if the signal is less than or greater than the carrier frequency. Amplitude modulated data is represented as a cosine (or sine) function (Eqn 1.4.1) .

$$F(t) = \sum_i \cos(2\pi\nu_i t)\ e^{-t/T_2} \quad \textbf{(1)}$$

From Euler's formula, the cosine function can be recast as the sum of two exponentials, which represent two vectors rotating in opposite directions.

$$\cos(2\pi\nu_i t) = \frac{1}{2}\left(e^{i2\pi\nu_i t} + e^{-i2\pi\nu_i t}\right) \quad \textbf{(2)}$$

The Fourier transform of this data (Eqn. 1.4.2) is,

$$S(\mathrm{v}) = \int_0^\infty \frac{1}{2}\cos(2\pi \mathrm{v}_i t)\; e^{-t/T_2}\; e^{i2\pi \mathrm{v}_0 t} \tag{3}$$

where decay of the FID is represented by the exponential containing T_2. Solution of this Fourier integral is easily accomplished with the substitution of Equation 8.4.2 into Equation 8.4.3

$$S(\mathrm{v}) = \int_0^\infty \frac{1}{2}(e^{i2\pi \mathrm{v}_i t} + e^{-i2\pi \mathrm{v}_i t})\; e^{-t/T_2}\; e^{i2\pi \mathrm{v}_0 t} \tag{4}$$

Expanding to a sum of integrals, we obtain Equation 8.4.5.

$$\begin{aligned} S(\mathrm{v}) = {} & \frac{1}{2}\int_0^\infty e^{i2\pi \mathrm{v}_i t}\; e^{-t/T_2}\; e^{i2\pi \mathrm{v}_0 t}\, dt \\ & + \frac{1}{2}\int_0^\infty e^{-i2\pi \mathrm{v}_i t}\; e^{-t/T_2}\; e^{i2\pi \mathrm{v}_0 t}\, dt \end{aligned} \tag{5}$$

As above, these integrals give,

$$\begin{aligned} S(\mathrm{v}) = \frac{1}{2}\Big[& \frac{T_2}{1 + (2\pi\Delta \mathrm{v} T_2)^2} - i * \frac{2\pi\Delta \mathrm{v} T_2^2}{1 + (2\pi\Delta \mathrm{v} T_2)^2} \\ & + \frac{T_2}{1 + (2\pi\Sigma \mathrm{v} T_2)^2} - i * \frac{2\pi\Sigma \mathrm{v} T_2^2}{1 + (2\pi\Sigma \mathrm{v} T_2)^2} \Big] \end{aligned} \tag{6}$$

where $\Delta \mathrm{v} = \mathrm{v}_0 - \mathrm{v}_i$ and $\Sigma \mathrm{v} = \mathrm{v}_0 + \mathrm{v}_i$. The absorption terms (the 1st and 3rd terms) are positive Lorentzian lines centered at $\pm \mathrm{v}_i$; the relative sign of the signal with respect to the carrier frequency is undetermined.

A similar result is obtained if the signal is detected along the X axis, however now the signal is represented as

$$F(t) = \sum_i \sin(2\pi v_i t)\ e^{-t/T_2} \tag{7}$$

Again by applying Euler's formula we obtain,

$$\sin(2\pi v_i t) = \frac{1}{2i}\ (e^{i2\pi v_i t} - e^{-i2\pi v_i t}) \tag{8}$$

By substituting Equation 8.4.8 into 8.4.7 and perfoming the Fourier transform we obtain Equation 8.4.9,

$$S(v) = \frac{1}{2i}\ [\ \frac{T_2}{1 + (2\pi \Delta v T_2)^2} - i * \frac{2\pi \Delta v T_2^2}{1 + (2\pi \Delta v T_2)^2} - \frac{T_2}{1 + (2\pi \Sigma v T_2)^2} + i * \frac{2\pi \Sigma v T_2^2}{1 + (2\pi \Sigma v T_2)^2}\ ] \tag{9}$$

The absorption terms (the 1st and 3rd terms) are Lorentizian lines centered at $\pm v_i$, however, these two peaks are opposite in sign. It is apparent that by combining the imaginary parts from Equation 2 with the real parts of Equation 1 that the term containing Σv is canceled; the absolute frequency of v is determined.