Signal Analysis in NMR: How Fourier Transform works

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ABSTRACT: Fourier transform in NMR spectroscopy plays a crucial role in transforming FID (Free Induction Decay) signal to frequency domain spectrum. Learning principle of Fourier transform in NMR helps people a lot in understanding the process of signal analysis and mastering skills of modifying signals to achieve better resolution, which is very important for all NMR researchers. However, most people doing NMR today usually treat Fourier transform no more than a mathematic tool and pay little attention on it, especially the basic principle part. In this paper, we focus on the basic principle of Fourier transform in NMR, including traditional continuous Fourier transform and advanced fast Fourier transform. Also, to make it more understandable, we use Mathematics, a powerful software, to build several demonstrations which are very friendly to use and explain the theory vividly. In these demonstrations, people can create initial FID signal by changing different parameters and the corresponding spectrum after Fourier transform will be automatically shown with initial FID. Furthermore, some window functions and noise are added in these demonstrations so that people can use them to modify the spectrum. In this paper, we also do some research on time-efficiency of Fourier transform. By comparison between continuous Fourier transform and discrete Fourier transform, we show the great power discrete Fourier transform has to analysis NMR signal.

KEY WORDS: signal analysis; Fourier transform; demonstration; time efficiency

INTRODUCTION

Fourier transform has been a powerful analytical tool to deal with linear systems, probability theory, quantum theory and signal analysis for a long time.[1-4] In NMR, Fourier transform cannot be more important since it plays an important role in converting original FID (Free Induction Decay) signal to frequency domain spectrum. With some knowledge of history of NMR, it is surprising to notice that the development of NMR techniques was somehow limited by the development of Fourier transform analysis method. According to the historical record, the NMR method didn't become popular until the appearance of fast Fourier transform (FFT), which is more efficient and timesaving. Fast Fourier transform is based on the discrete Fourier transform and it was first developed by Cooley and Tukey in 1965.[5] It is a computational algorithm that reduces the computing time and quickly had completely revolutionized many facets of scientific analysis, including signal analysis in NMR. However, in recent years, most people doing NMR treat

Fourier transform no more than a mathematic tool and pay little attention on it, which will definitely limit the development of knowledge on NMR techniques. To help people better understand the basic principle and the application of Fourier transform, in this paper, a very brief introduction about the Fourier transform in NMR is presented and also we use Mathematics demonstrations to clearly show the whole process of Fourier transform. In this article, we only consider the case of a single spin-1/2 particle in a static magnetic field.

BASIC THEROY OF FOURIER TRANSFORM[6]

In mathematics, the Fourier transform is defined as

$$S(f) = \int_{-\infty}^{\infty} s(t)\exp\,[-ift]dt$$

Where $s(t)$ is a function of variable time. $S(f)$ is the Fourier transform of $s(t)$ and it is a function of variable frequency.

Since an imaginary part is involved in this presentation, more generally, the Fourier transform can also be shown as:

$$S(f) = R(f) + iI(f) = |H(f)|e^{i\theta(f)}$$

Where $R(f)$ is the real part of the Fourier transform. $I(f)$ is the imaginary part of the Fourier transform. $|H(f)|$ is the amplitude of Fourier transform spectrum of $S(f)$ and is given by $\sqrt{R^2(f) + I^2(f)}$. $\theta(f)$ is the phase angle of the Fourier transform and is given by $\tan^{-1}[\frac{I(f)}{R(f)}]$. Generally, suppose we have a function of variable time

$$S(t) = \begin{cases} a\exp[-bt] & t > 0 \\ 0 & t < 0 \end{cases}$$

By applying the Fourier transform above, we have

$$\begin{aligned} S(f) &= \int_0^{\infty} a\exp\,[-bt]\exp\,[-ift]dt \\ &= a\int_0^{\infty} \exp\,[-bt - ift]dt \\ &= \frac{a}{b + if} = \frac{ab}{b^2 + f^2} - i\frac{af}{b^2 + f^2} \end{aligned}$$

After Fourier transform, the function of variable time has been transformed to the function of variable frequency with real and imaginary components.

FID OF NMR

Since Fourier transform in NMR is applied to transform FID signal to frequency domain spectrum, before discussing details about Fourier transform in NMR, first, we need to have a basic idea of what FID signal is.

Basically, NMR is based on pulse and magnetization relaxation in the spin system. Suppose we applied one simplest pulse, $(\frac{\pi}{2})_x$ pulse. Following that pulse, the spin system is left to relax and signal is recorded. The signal is called Free Induction Decay (FID). There are two kinds of relaxation during that period, one is spin-lattice relaxation and the other is spin-spin relaxation. The former one is along the z-axes and is called T_1 relaxation while the latter one is in the x-y plane and is called T_2 relaxation. If we ignore the relaxation, the magnetizations along the x, y, z axes can be described with Bloch equation and shown below as

$$M_x(t) = M_x(0)cos\omega^0 t + M_y(0)sin\omega^0 t$$

$$M_y(t) = M_x(0)sin\omega^0 t - M_y(0)cos\omega^0 t$$

$$M_z(t) = M_z(0)$$

Where $M_x(0)$, $M_y(0)$ and $M_z(0)$ is the magnetization along the x, y, z axes at the initial time, respectively.

However if we take the relaxation into consideration, we will have

$$M_x(t) = [M_x(0)cos\omega_0 t + M_y(0)sin\omega_0 t]e^{-\frac{t}{T_2}}$$

$$M_y(t) = [M_y(0)cos\omega_0 t - M_x(0)sin\omega_0 t]e^{-\frac{t}{T_2}}$$

$$M_z(t) = M_z(0)e^{-\frac{t}{T_1}} + M_0(1 - e^{-\frac{t}{T_1}})$$

Where M_0 is the magnetization of the equilibrium state while T_1 and T_2 are spin-lattice relaxation time and spin-spin relaxation time respectively.

Since we assume that a $(\frac{\pi}{2})_x$ pulse is applied to the system, then

$$M_x(0) = 0, M_y(0) = M_0, M_z(0) = 0$$

So the previous result can be rewrite to the forms below:

$$M_x(t) = [M_0 sin\omega_0 t]e^{-\frac{t}{T_2}}$$

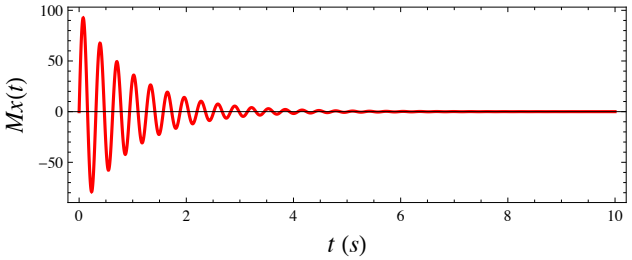
$$M_y(t) = [M_0 cos\omega_0 t]e^{-\frac{t}{T_2}}$$

$$M_z(t) = M_0(1 - e^{-\frac{t}{T_1}})$$

If we set $M_0 = 100, \omega_0 = 20Hz, T_1 = 2s, T_2 = 1s$, we can plot out the three magnetization. (See Figure 1)

Since the detecting coil can only observe the change of magnetization in the x-y plane, the FID signal is made up of x and y component of magnetization. The final representation of NMR signal is shown as

$$S(t) = M_y(t) + iM_x(t) = M_0 \exp\left[\left(i\omega_0 - \frac{1}{T_2}\right)t\right]$$



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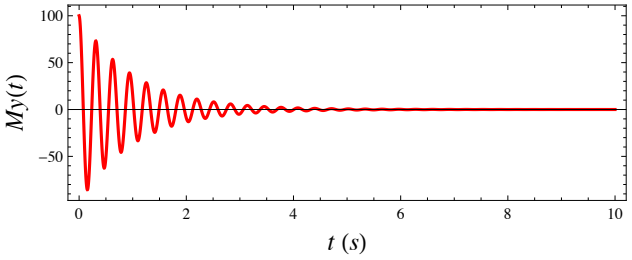

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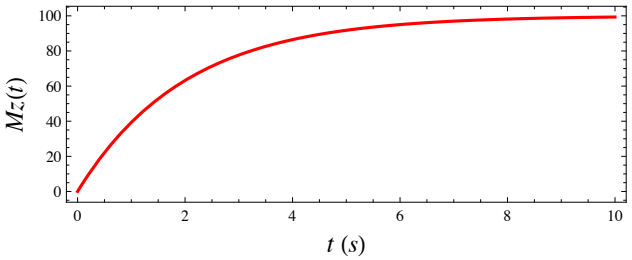


(C)

Figure 1 Plots of (A) $M_x(t)$, (B) $M_y(t)$, (C) $M_z(t)$ for $M_0 = 100, \omega_0 = 20Hz, T_1 = 2s, T_2 = 1s$.

If we assume $\frac{1}{T_2} = \lambda$, then

$$S(t) = M_0 \exp\left[(i\omega_0 - \lambda)t\right]$$

$M_y(t)$ is the real part of the FID signal and $M_x(t)$ is the imaginary part of the FID signal.

From the representation of original FID signal, it is easy to find that the signal is a function of variable time, which cannot tell difference between different nucleuses precessing at different frequencies. The best way to solve this problem is to apply Fourier transform to obtain a frequency domain spectrum. In

that way, we can get information about the nucleus with different chemical environment.

FOURIER TRANSFORM IN NMR[6]

Since we have already known the basic principle of Fourier transform and the representation of FID signal in NMR, we are going to do Fourier transform on the signal.

By applying Fourier transform on the signal

$$S(\omega) = \int_0^\infty s(t)\exp\{-i\omega t\}dt$$

After replacing $S(t)$ with $\exp[(i\omega_0 - \lambda)t]$, we have

$$\begin{aligned} S(\omega) &= \int_0^\infty M_0 \exp[(i\omega_0 - \lambda)t]\exp\{-i\omega t\}dt \\ &= M_0 \int_0^\infty \exp[i(\omega_0 - \omega)t - \lambda t]\,dt \\ &= \frac{M_0}{i(\omega_0 - \omega) - \lambda}\exp[i(\omega_0 - \omega)t \\ &\quad - \lambda t]\,|_0^\infty = 0 - \frac{M_0}{i(\omega_0 - \omega) - \lambda} \\ &= \frac{M_0}{\lambda + i(\omega - \omega_0)} \end{aligned}$$

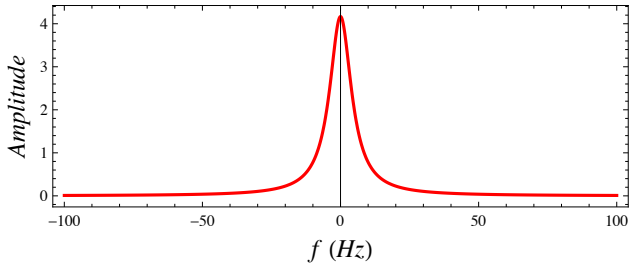
This is the complex Lorentzian form. We can further separate the form into two parts; one is the real part while the other is the imaginary part.

$$\begin{aligned} \frac{M_0}{\lambda + i(\omega - \omega_0)} &= \frac{\lambda}{\lambda^2 + (\omega - \omega_0)^2}M_0 \\ &\quad - \frac{(\omega - \omega_0)}{\lambda^2 + (\omega - \omega_0)^2}M_0 \end{aligned}$$

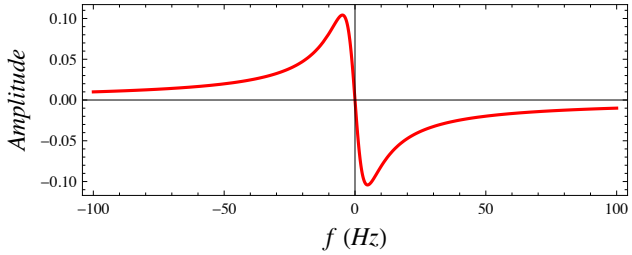
The real part of the complex Lorentzian is called the absorption Lorentzian:

$$A = \frac{\lambda}{\lambda^2 + (\omega - \omega_0)^2}$$

The imaginary part of the complex Lorentzian is called the dispersion Lorentzian:



(A)



(B)

Figure 2 Plots of absorption (A) and dispersion (B) Lorentzian peaks.

$$D = -\frac{(\omega - \omega_0)}{\lambda^2 + (\omega - \omega_0)^2}$$

If we assume that

$$L = \frac{1}{\lambda + i(\omega - \omega_0)}$$

Then we have

$$L = A + D$$

If we set $\lambda = 1$, $\omega_0 = 0$, we can plot out absorption Lorentzian and dispersion Lorentzian. (Figure 2)

From that, we know that the signal peak in NMR is a Lorentzain peak. The result we have derived is the analytical result for Fourier transform, which needs less time to calculate out. However, in fact, for complex spin system, the expression of Fourier transform is much more complicated. Hence, deriving

its analytical representation is very difficult. So the only way for computer to do is to derive the numerical solution, which is more time consuming and less efficient. This had been a problem for development of NMR for a really long time until the appearance of fast Fourier transform, which makes it possible for computer to do Fourier transform. In this paper, we used Mathematics to show the time efficiency of fast Fourier transform and compare it with traditional continuous Fourier transform. Before doing that, we need to learn some basic theory of fast Fourier transform.

FAST FOURIER TRANSFORM

Basically, the fast Fourier transform (FFT) is based on the discrete Fourier transform and it is simply an algorithm that can compute the discrete Fourier transform much more rapidly than other available algorithms. The discrete Fourier transform is defined by the formula

$$X(n) = \sum_{k=0}^{n-1} x_0(k) e^{-i2\pi nk/N} \quad n = 0,1,\dots,N-1$$

Actually, there are many FFT algorithms to compute the discrete Fourier transform and its inverse, such as Cooley-Tukey algorithm, Prime-factor algorithm, Bruun's algorithm, Rader's algorithm and Bluestein's algorithm. Cooley-Tukey algorithm, which is first published by Cooley and Tukey, is the most widely used algorithm. Its basic principle is to divide the transform into two parts of N/2 size at each step and generally break the full discrete Fourier transform into smaller discrete Fourier transform. More information about other kinds of algorithms and FFT can be found in these references. [7-12]

To be more simple and understandable, we simply applied discrete Fourier transform to analyze simple systems in following demonstrations since these systems do not involve large amounts of data points.

MATHEMATICS DEMONSTRATIONS

In this part, we applied the powerful software Mathematic to build several demonstrations to clearly show all the nice feathers of Fourier transform in NMR signal transformation.

(I) Fourier transform of single signal

The major parameters we set for the signal in the Mathematics list below: a) delay time; b) acquisition time; c) number of data points; d) amplitude; e) peak position (chemical shift); f) initial phase; g) T_2 relaxation time (spin-spin relaxation time). The reason why we choose acquisition time and spectrum width is that we think these two parameters can be directly observed from the FID display and spectrum window. Several relevant parameters can be derived from all the parameters shown previously. For example, dwell time can be easily calculated from number of data points, [dwell time = acquisition time / number of data points]. One thing to keep in mind is that in the real case dwell time should not be too large, so always keep [acquisition time/number of data points] small.

Besides setting signal parameters, also, we set some manipulating parameters to optimize the signal or modify the signal, such as phase correction and window function. Since window function is really important in NMR signal transformation, we set up five window functions in this demonstration to vividly show how important the role window functions play in signal manipulating. This demonstration is the first time to involve all the signal parameters and all kinds of window function people usually use to modify the signals. Another good feature is that both FID and spectrum after Fourier transform are displayed in the dynamic showing window. People can easily see how they are going to change with manipulation of parameters.

In display window, both real and imaginary parts are displayed. People can easily see how these signal parameters determine the real and the imaginary components.

The Mathematic code is available in the supporting information.

(II) Fourier transform of multiple signals

We set three signals of different frequencies, and most of the parameters are the same as those in single signal case. In this demonstration, we set parameters for each signal, which means three amplitudes, three frequencies, and three T_2 relaxation times. However, we only display the real part of the FID and its corresponding spectrum since people can get idea of imaginary part from that single signal demonstration. In this demonstration, we can see how peaks overlap and how to manipulate the window functions to optimize the spectrum when going to the multiple signals situation. However, delay time and phase parameters are not included in this demonstration for the reason of time efficiency. The Mathematics code is available in the supporting information.

(III) Fourier transform of signals with noise component

In real NMR experiment, there is noise coming from instrument, usually we call it background. To better understanding the influence of noise to the signal, we write another demonstration to show vividly the process, which is very close to the real situation. The reason why we write a separated demonstration to show noise effect is that when noise is involved in the simulation, the time efficiency will become much lower and it challenges computer to run the manipulation, which means it will take a lot of time when you just change one certain parameter. In order to show clearly all the features, we write two demonstrations, one is without noise component and has a high time efficiency while the other is with noise and may take some time to run manipulation.

We mainly set two parameters for noise component, amplitude of noise and transient. To be more accurate, transient is not a parameter only for noise, it is a special parameter in NMR experiment, since the signal noise ratio, which is a key parameter in every spectroscopy, can be optimized by increasing the transients, we add this parameter to the demonstration program to show this great feature.

We build two demonstrations in this part, one is for single signal and the other is for multiple signals. But to be more time efficient, we only use exponential window function in multiple signals demonstration while delay time and phase parameters are not included in this demonstration. The mathematic code is available in the supporting information.

TIME EFFICIENCY OF FOURIER TRANSFORM

Another great feature of Fourier transform in recent NMR is the high time-efficiency, which attribute to the Fast Fourier transform. In this paper, one of our goals is to compare the traditional continuous Fourier transform and the discrete Fourier transform, which is widely used today. In this way, we want to show how important the Fourier transform is when we get through a situation that contains a huge number of data points. The main method we use here is to apply both kinds of Fourier transforms on the same signal and all calculation is done on the same computer. The time used for the transformation process was calculated by computer program and we plot out the relationship between the time it take and the number of data points we set.

The signal function we use in this experiment is shown below

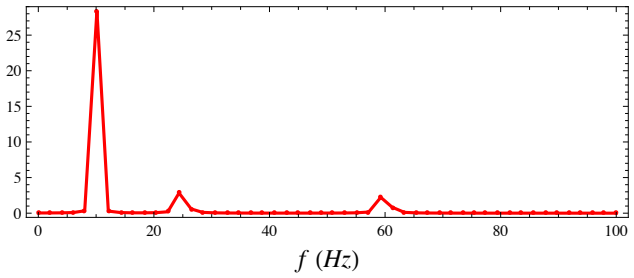
$$S(t) = M_0 \exp[(i\omega_1 - \lambda)t] + M_0 \exp[(i\omega_2 - \lambda)t] + M_0 \exp[(i\omega_3 - \lambda)t]$$

Where $M_0 = 100, \omega_1 = 10Hz, \omega_1 = 25Hz, \omega_1 = 60Hz, \lambda = \frac{1}{T_2}, T_2 = 1s.$

And also we set the acquisition time as 3s and dwell time can be obtain for each point with different number of points.

For traditional Fourier transform, the numbers of points we tested are 10, 15, 20, 30, 50, 100 and 200. For Fast Fourier transform, the numbers of points we tested are 300, 500, 1000, 1500, 2000, 3000, 5000, 10000 and 20000. All these experiments are done on MacBook Pro with 2.4GHz Intel Core i5 Processor and 4GB 1333MHz DDR3 Memory.

We showed several simulated pictures and the relationship between the time and number of data points was plot out in Figure 4 for both traditional continuous Fourier transform and discrete Fourier transform.



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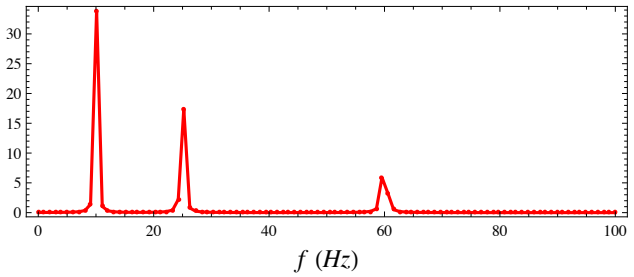

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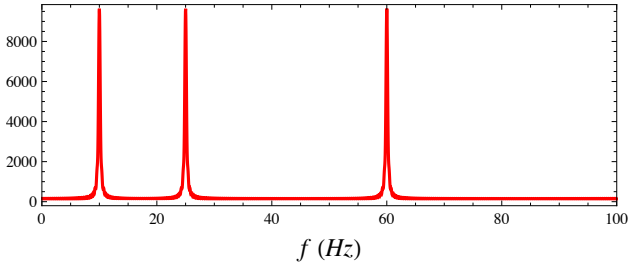

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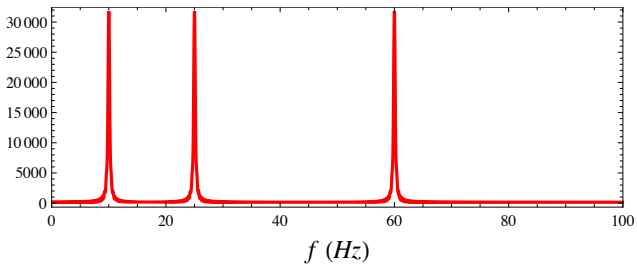
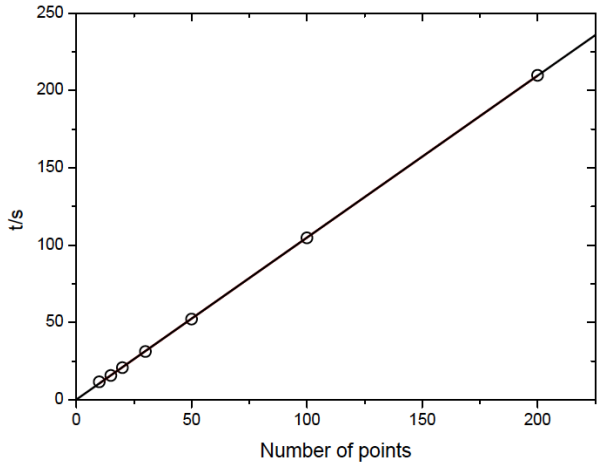
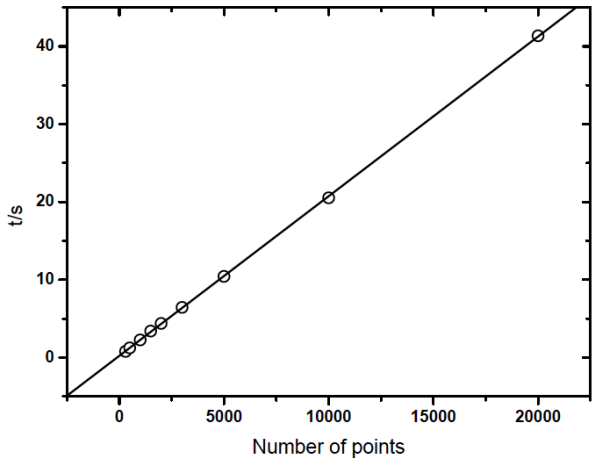


(D)

Figure 3 Simulated spectrums with continuous Fourier transform and fast Fourier transform. (A) continuous Fourier transform with 50 points; (B) continuous Fourier transform with 100 points; (C) discrete Fourier transform with 300 points; (D) discrete Fourier transform with 1000 points;



(A)



(B)

Figure 4 Plots of time for different number of points in continuous Fourier transform (A) and fast Fourier transform (B).

The time used in data analysis has linear relationship with the number of data points to be calculated. For continuous Fourier transform, it takes more than 200 seconds for 200 data points. However, for discrete Fourier transform, it only takes about 40 seconds for 20000 data points. It is well known that the more data points calculated, the more accurate the spectrum is. From the result, we can easy figure out that the discrete Fourier transform is much faster and more efficient than continuous Fourier transform. Discrete Fourier transform makes it possible for computer to analysis complicated FID signal within just a few seconds. Also, with fast Fourier transform, NMR can

be extended to two-dimensional and even multi-dimensional NMR.

CONCLUSION

In this paper, we mainly discuss the Fourier transform in NMR. We build several demonstrations to clearly show the process of signal analysis in NMR, including Fourier transform and window functions. Although continuous Fourier transform is a very important concept in mathematic and signal analysis, it can never be applied in NMR signal analysis because of low time-efficiency. With the application of fast Fourier transform, NMR stepped into a new era and it is widely believed that it is fast Fourier transform that makes NMR so popular used in recent research.

REFERENCE

1 Born, M. & Wolf, E. Principles of Optics. *New York: Pergamon Press* (1959).

2 French, A. P. Principle of Modern Physics. *New York: Wiley* (1961).

3 Gupta, S. C. Transform and State Variable Methonds in Linear Systems. *New York: Wiley* (1966).

4 Papoulis, A. Probability, Random Variables, and Stochastic Process. *New York: McGraw-Hill* (1965).

5 Cooley, J. W. & Tukey, J. W. An algorithm for the machine calculation of complex Fourier series. *Mathematics of Computation* **19**, 5 (1965).

6 Levitt, M. H. Spin Dynamics. *John Wiley & Sons. Ltd*.

7 Bruun, G. z-Transform DFT filters and FFTs. *IEEE Trans. on Acoustics, Speech and Signal Processing* **26**, 8 (1978).

8 Rader, C. M. Discrete Fourier transform when the number of data sample is prime. *Proc. IEEE* **56**, 2 (1968).

9 Leo I, B. A linear filtering approach to the computation of the discrete Fourier transform. *Northeast Electronics Research and Engineering Meeting Record* **10**, 2 (1968).

10 Elliot, D. F. & Rao, K. R. Fast Fourier Transforms: Algorithms. *Academic, New York* (1982).

11 Walker, J. S. Fast Fourier Transforms. *CRC Press* (1996).

12 Brigham, E. O. The Fast Fourier Transform. *New York: Prentice-Hill* (1974).