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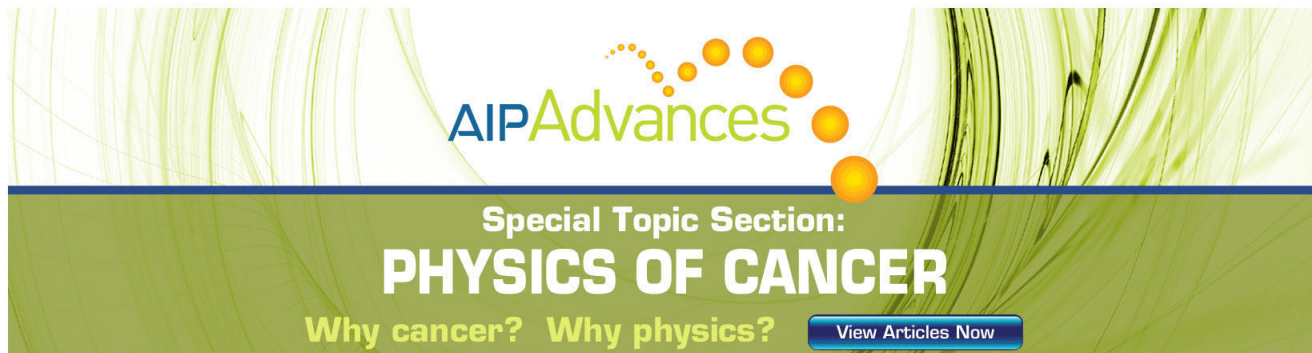
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Magnetic resonance spectral reconstruction using frequency-shifted and summed Fourier transform processing

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A novel method of Fourier transform spectroscopy of the transient signals from wide, inhomogeneously broadened magnetic resonance spectra is described and analyzed. It has the advantages of high resolution, high sensitivity, and freedom from the distortions introduced by the finite amplitude of the pulsed rf magnetic field and the finite bandwidth of the receiving system. It consists of recording the transient signal at a series of magnetic fields, shifting the frequency of the transient by the corresponding field step for each point, and summing the corresponding Fourier transformed signals. Although the primary emphasis is on pulsed NMR, the analysis also applies to pulsed ESR. Criteria for the range and step interval of the magnetic field variation are discussed. The accuracy and sensitivity of the method are compared with earlier methods of spin echo spectroscopy. A description of the corresponding measurement of NQR, NMR, and ESR spectra obtained by stepping the frequency of the spectrometer is also presented. © 1995 American Institute of Physics.

I. INTRODUCTION

One of the central problems in pulsed magnetic resonance (MR) spectroscopy of solids is to measure the absorption spectrum of a line that has a very large inhomogeneous broadening. It arises in nuclear magnetic resonance (NMR), in electron spin resonance (ESR), and in the related field of nuclear quadrupolar resonance (NQR). In principle, such a spectrum in the frequency domain can be obtained from the Fourier transform of the free induction decay (FID) signal at a single value of the magnetic field. Several circumstances often make this approach impractical: (1) The rf magnetic field (B_1) is not large enough to excite the entire spectrum, (2) the bandwidth and phase shift of the circuit into which the processing magnetic signal is induced¹ (magnetic induction circuit) distorts the signal, (3) frequency dependent phase shifts and the finite bandwidth of the receiving system further modify the detected signal, and (4) when a large value of B_1 is used, the corresponding free induction decay signal has such a short lifetime that it is lost in the dead time of the receiving system. When B_1 is large enough to access all of the spins, the problem of the receiver dead time can often be circumvented by recording a spin echo in the time domain and calculating the Fourier transform of either the full echo or its second half when it is a replica of the FID, as is often the case. This approach does not, however, remove the undesired phase shifts and bandwidth limitations associated with the circuit that picks up the transient signal and its subsequent amplification and detection in the receiving system.

Two types of spin echo spectroscopy are alternatives to obtain the MR spectrum of a very wide, inhomogeneously broadened line. One of them, spin echo height spectroscopy (SEHS), has been used in NMR investigations for many years.²⁻⁵ It is implemented by measuring the height of the

spin echo as a function of the magnetic field. The basis of this technique, which is analyzed in more detail below, is to form a spin echo with a value of B_1 that is small compared to the width in magnetic field of any feature of the spectrum that is to be recorded. Roughly speaking, the spins within B_1 of resonance contribute to the height of the spin echo. By sweeping the magnetic field through the MR spectrum and recording the height of the spin echo at each point, the MR absorption line shape is obtained. A major shortcoming of this method is the corresponding loss of sensitivity that occurs because the small value of B_1 limits the number of spins contributing to each spin echo signal. Despite these limitations, many useful NMR spectra have been obtained using this method. A significant advantage over measuring just the height of the spin echo is obtained by measuring its integrated area. We shall refer to this method as spin echo integration spectroscopy (SEIS).

A variant of SEHS and SEIS in which one sweeps the frequency is sometimes used to record NMR spectra when a field sweep is not available and to measure NQR spectra. Even though this application introduces the added complication of the changing frequency response of the spectrometer and the magnetic induction circuit, it has, nevertheless, been used successfully.

In this paper we describe an alternative method for obtaining the absorption spectrum of a wide, inhomogeneously broadened MR line. The method is compatible with the largest value of B_1 available and it includes the correction for the response of the spins away from resonance as well as the phase shifts and finite frequency response of the magnetic induction circuit and receiving systems. Thus it benefits from the signal of the maximum number of spins that can be tipped by B_1 and it corrects the various distortions caused by

the MR spectrometer system. We will refer to it as the frequency step and sum (FSS) method. It consists of recording the transient signal at a series of magnetic fields, shifting the frequency of the transient by the corresponding field shift for each point, and summing the corresponding Fourier transformed signals. Although the main purpose of the method is to obtain an accurate spectrum and high sensitivity when there is a large inhomogeneous broadening, it is often useful when only a moderate amount of inhomogeneous broadening is present. Our discussion does not include the complications of spectral diffusion or a finite spin-lattice relaxation time (T_1), but the effect of the spin-spin relaxation time (T_2) is included phenomenologically provided it is the same for all parts of the spectral line and long compared to the observed free induction decay time (T_2^*). Although the description and analysis is done specifically for the pulsed NMR case, the same considerations apply for pulsed ESR.

A brief description of the related cases of pulsed NQR and pulsed MR without a field sweep is also presented. It is more difficult to implement because the spectrum is traversed by stepping the frequency of the spectrometer, with the consequence that the overall system response changes during the measurement. Strategies to mitigate this difficulty are described.

The existence of the FSS method was brought to the attention of one of us (W.G.C.) by H. Brom of Leiden, who pointed out a short passage in a paper from the group of Michael Mehring in Stuttgart which mentioned that a spectrum had been obtained in this way.⁶ To the best of our knowledge, no analysis of the method exists in the literature. The motivation for this paper is, therefore, to make the analysis of it widely available and to avoid the circumstance that it diffuse slowly into the research community simply as "common knowledge."

The rest of this paper is organized as follows: The next section states the most important Fourier transform relations that are used for the analysis and describes the model used for the NMR signal and the way it is modified by the finite B_1 , the NMR coil system, and the receiving system. It is followed by a brief discussion of the SEHS and SEIS methods. Then the field-stepped FSS method is described and analyzed, including a rough comparison with SEHS. Finally, a practical application of the method is discussed and a brief description of the frequency-stepped FSS case is presented.

II. FOURIER ANALYSIS AND THE DETECTED MR SIGNAL

Here we present the notation that will be used for the Fourier transform properties used in this paper. It follows closely that of Brigham.⁷ In general we use capitalized functions to indicate the frequency (f) domain and lower case functions for the corresponding transform in the time (t) domain. The definition used for the forward and inverse transforms are

$$h(t) = \int_{-\infty}^{\infty} H(f) e^{i2\pi ft} df \quad (1)$$

and

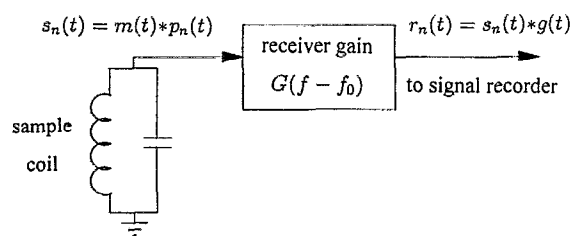


FIG. 1. Simplified pulsed NMR receiving circuit. The transient NMR signal $s_n(t)$ at the field $B_0 + \Delta B_n$ with the Fourier transform $M(f)P_n(f) \Leftrightarrow m(t)p_n(t)$ is generated at the input of the receiver. It differs from the undistorted NMR spectrum because the rf pulse is not a pure impulse (B_1 is finite) and because of the frequency dependent response of the NMR coil system. The response $r_n(t)$ at the output of the receiving system is further modified by the frequency dependent gain of the receiver.

$$H(f) = \int_{-\infty}^{\infty} h(t) e^{-i2\pi ft} dt. \quad (2)$$

The following notation will be used to indicate that two quantities are Fourier transforms, as indicated by Eqs. (1) and (2):

$$H(f) \Leftrightarrow h(t). \quad (3)$$

Use will be made of the frequency shifting relation for Fourier transform pairs,

$$h(t) e^{i2\pi f_0 t} \Leftrightarrow H(f - f_0), \quad (4)$$

as well as the impulse function (Dirac delta function) $\delta(t)$, which has the representation

$$\delta(t) = \int_{-\infty}^{\infty} e^{i2\pi ft} df, \quad (5)$$

and the property that the Fourier inverse transform of the product, $A(f)B(f)$, of two functions in the frequency domain is the convolution of their inverse transforms in the time domain; i.e.,

$$a(\tau) * b(\tau) = \int_{-\infty}^{\infty} a(t)b(t-\tau) dt \Leftrightarrow A(f)B(f), \quad (6)$$

where the operation "*" is used to denote convolution.

Now we describe the transient signal and the key elements of the spectrometer that generates and processes it using field-stepped NMR as an example. The essential parts of the receiving system are shown in Fig. 1. They are the tuned NMR coil circuit that picks up the transient NMR signal $s_n(t)$ and the receiver, which amplifies and detects the signal to provide an output transient $r_n(t)$, where the subscript n indexes the n th value of the magnetic field at which the signal is recorded. Subsequent processing of the signal usually involves mixing the signal with a reference frequency (multiplication of the two waveforms) to translate the signal to a much lower frequency for further modification and processing. For the purpose of this paper, we will consider that all of these subsequent steps are translated back to the original signal frequency and that their effects are represented by the properties of the receiver. From a practical

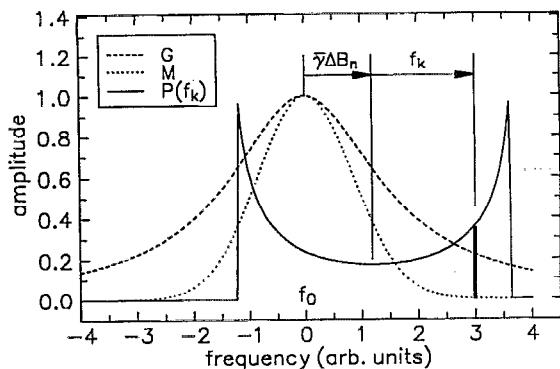


FIG. 2. Schematic representation of the responses in the frequency domain. The solid line is a model field shifted MR absorption signal $P(f)$ and the heavy vertical line is one isochromat shifted by the frequency f_k from a fixed point on the line. The dashed line is proportional to the real part of the receiver gain G centered at f_0 and the dotted line is the real part of the effective MR response M that depends on the size of B_1 and the electrical response of the receiving coil circuit. For the condition shown, the center of the MR line is offset by the frequency $\bar{\gamma}\Delta B_n$. For the field-stepped FSS method, the MR signal is stepped past G and M by changing the magnetic field.

point of view, this means that all bandwidth control and phase shifts are treated as if they occurred at the high frequency in the receiver.

Figure 2 indicates schematically the relevant quantities in the frequency domain. A broad NMR absorption spectrum is indicated by the curve labeled by its distribution $P(f_k)$, where f_k is the frequency from a reference point on the spectrum, which in this case has been chosen at the center of the spectrum. The value of f_k is determined by the applied magnetic field B . The inhomogeneously broadened line is considered a superposition of narrow spin packets (isochromats) with a weight $P(f_k)$ indicated by the thick vertical line. The measuring field B_n for the n th measurement is given by

$$\bar{\gamma}B_n = \bar{\gamma}B_0 + \bar{\gamma}\Delta B_n = f_0 + \bar{\gamma}\Delta B_n, \quad (7)$$

where f_0 is the frequency to which the receiver is tuned, $\bar{\gamma}$ the nuclear gyromagnetic ratio in MHz/T,⁸ and $\bar{\gamma}\Delta B_n$ is the frequency difference between the spectrum reference point and f_0 . The frequency f_0 is that of the reference frequency generator used for phase coherent detection. As B is varied, the spectrum $P(f)$ is swept past f_0 .

The NMR signal is amplified and detected with a linear, phase coherent receiving system whose frequency response $G(f-f_0)$ is centered at f_0 . Its real part is indicated in Fig. 2 by the corresponding bell-shaped curve (dashed line).

One of the key elements of analyzing a very broad NMR spectrum is the effect of an rf field amplitude B_1 that is substantially smaller than the width of the spectrum. Consideration of the spin motion in the rotating frame shows that, roughly speaking, B_1 nutates those spins within about B_1 of resonance into the plane perpendicular to the applied field, but that spins farther away from resonance are left in an orientation that depends on their distance from resonance.⁹ Thus the subsequent NMR signal depends upon the amplitude and phase of each processing isochromat at the end of the rf pulse. In addition, the signal induced in the receiving coil circuit by the processing isochromat will depend upon

the gain and phase shift of the circuit at the frequency of the isochromat. Here, the combination of these effects is modeled with a complex, frequency dependent term $M(f-f_0)$ centered at f_0 that multiplies the signal induced in the NMR coil by each processing isochromat. Its real part is shown schematically in Fig. 2 by the dotted line. Under these circumstances, the signal for one isochromat at the input of the receiver, $s_n(f_k, t)$, is

$$s_n(f_k, t) = P(f_k)M(\bar{\gamma}\Delta B_n + f_k)e^{i2\pi(f_0 + \bar{\gamma}\Delta B_n + f_k)t}e^{-t/T_{2k}}, \quad (8)$$

where the term $\exp(-t/T_{2k})$ represents phenomenologically the spin-phase relaxation time of the given isochromat. Its effect is to form a convolution in the frequency domain [Eq. (6)] of a Lorentzian of width $1/\bar{\gamma}T_{2k}$ with the product $P(f_k)M(\bar{\gamma}\Delta B_n + f_k)$. In the analysis that follows, we will assume that T_{2k} is the same for all k and that it is long enough that it has a negligible effect on the shape of the NMR spectrum in the frequency domain. Under these circumstances, its effect on the spectrum is simply that of a multiplicative constant. It will be dropped from further consideration in this paper.

At the output of the receiver the signal is multiplied by the receiver response to give

$$\begin{aligned} r_n(f_k, t) &= s_n(f_k, t)G(\bar{\gamma}\Delta B_n + f_k) \\ &= P(f_k)G(\bar{\gamma}\Delta B_n + f_k) \\ &\quad \times M(\bar{\gamma}\Delta B_n + f_k)e^{i2\pi(f_0 + \bar{\gamma}\Delta B_n + f_k)t}. \end{aligned} \quad (9)$$

The signal from all of the isochromats is then

$$\begin{aligned} r_n(t) &= e^{i2\pi(f_0 + \bar{\gamma}\Delta B_n)t} \int_{-\infty}^{\infty} P(f_k)G(\bar{\gamma}\Delta B_n + f_k) \\ &\quad \times M(\bar{\gamma}\Delta B_n + f_k)e^{i2\pi f_k t} df_k. \end{aligned} \quad (10)$$

Equation (10) illustrates the central problem of obtaining the NMR absorption spectrum $P(f_k)$. The Fourier transform of the signal in the time domain is the product of $P(f_k)$ with the usually unknown functions $G(\bar{\gamma}\Delta B_n + f_k)$ and $M(\bar{\gamma}\Delta B_n + f_k)$ centered at $f_0 + \bar{\gamma}\Delta B_n$. To find $P(f_k)$ requires an inversion to remove $G(\bar{\gamma}\Delta B_n + f_k)M(\bar{\gamma}\Delta B_n + f_k)$. It is this inversion that is accomplished with the FSS method.

III. FIELD-STEPPED SPIN ECHO HEIGHT SPECTROSCOPY

Before discussing the FSS method, it is instructive to consider semiquantitatively the small B_1 limit of SEHS. In this case, the width of $M(\bar{\gamma}\Delta B_n + f_k)$ is approximately $\bar{\gamma}B_1$. Since it is very narrow, we approximate M by the impulse function

$$M(\bar{\gamma}\Delta B_n + f_k) \approx A \delta(\bar{\gamma}\Delta B_n + f_k), \quad (11)$$

where A is a constant. When this substitution is made in Eq. (10) and the integration carried out, the result

$$r_n(t) \approx AP(-\bar{\gamma}\Delta B_n)G(0)e^{i2\pi f_0 t} \quad (12)$$

is obtained. Equation (12) shows that the height of the signal at $t \rightarrow 0$ (or the corresponding height of the spin echo formed at twice the pulse spacing) is proportional to the intensity of

the absorption spectrum at $-\bar{\gamma}\Delta B_n$. Thus SEHS does give the amplitude of the spectrum at each measurement point $-\bar{\gamma}\Delta B_n$, but it suffers in sensitivity because only a small fraction of the total number of spins participates in the signal.

As B_1 is increased, it is readily shown that the Fourier transform of $r_n(t)$ is a weighted average of $P(-\bar{\gamma}\Delta B_n)$ over the range approximately equal to $\pm\bar{\gamma}B_1$.

IV. FIELD-STEPPED SPIN ECHO INTEGRAL SPECTROSCOPY

Now we discuss briefly the SEIS method when using a stepped magnetic field. It is equivalent to the method of integrating the FID reported earlier¹⁰ when the echo has the same functional form as the FID. Frequently, however, it is difficult to obtain an undistorted integral of the FID because of the receiver dead time and other effects, as discussed by Avogadro *et al.*¹¹ The main advantage of integrating the echo instead of the FID is that for the echo the dead-time problem is usually avoided. Despite this problem with the FID, acceptable spectra have been obtained by integrating it when its duration is not too short.¹²

In order to simplify the analysis, we consider the case in which the real part of echo signal after detection is an even function of time about its center and its imaginary part is odd.¹³ We will also assume that the *entire* echo waveform is integrated. As before, the signal from all of the isochromats is given by Eq. (10). Then, the integral of the echo signal is

$$\int_{-\infty}^{\infty} r_n(t) dt = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} df_k dt P(f_k) G(\bar{\gamma}\Delta B_n + f_k) \times M(\bar{\gamma}\Delta B_n + f_k) e^{i2\pi(f_0 + \bar{\gamma}\Delta B_n + f_k)t}. \quad (13)$$

Since the integral over time is $\delta(f_0 + \bar{\gamma}\Delta B_n + f_k)$, the integral over f_k sets $f_k = -(f_0 + \bar{\gamma}\Delta B_n)$. Thus

$$\int_{-\infty}^{\infty} r_n(t) dt = P(-f_0 - \bar{\gamma}\Delta B_n) G(-f_0) M(-f_0). \quad (14)$$

For excitation by a linearly polarized rf magnetic field, all of the functions are even about zero frequency, so that

$$\int_{-\infty}^{\infty} r_n(t) dt = P(f_0 + \bar{\gamma}\Delta B_n) G(f_0) M(f_0). \quad (15)$$

This result shows that the average of the echo (or FID) is the absorption signal at a single frequency and that it is independent of the structure of the response functions $G(f)$ and $M(f)$. It also shows that one can use the largest B_1 available to maximize the signal amplitude. In both of these ways it is superior to the SEHS method. Since, however, it is the spectrum at a single frequency, a large number of points must still be measured to obtain a spectrum that is rich in structure. In this sense it is less powerful than performing a Fourier transform on the same signal because the Fourier transform provides many frequencies from the same measurement.

If only part of the echo (or FID) is integrated to improve the signal-to-noise ratio,¹¹ it can be shown that instead of the spectrum at a single frequency, the measurement is a

weighted average of the NMR spectrum over a range of frequencies whose width is approximately the inverse of the time interval over which the integration is done. Although we do not discuss it further here, the SEIS method can also be adapted to frequency stepping, but with the complication that a variation in G and M with f_0 may complicate the analysis.

V. THE FIELD-STEPPED FSS METHOD

Now we discuss the field-stepped FSS method for the NMR example. To improve the sensitivity of the measurement, a large value of B_1 is used to incorporate as many spins as possible into the echo signal. If necessary, the sensitivity can be enhanced by averaging the result over many signals obtained at the same magnetic field. It will be assumed that phase coherent detection is used with a reference frequency $f_0 = \bar{\gamma}B_0$, where B_0 is a value of the magnetic field near the center of the NMR absorption line.

A key assumption of the analysis will be that the recorded signal captures the entire transient signal of the processing nuclei. Because of the dead time usually present in a real spectrometer after an rf pulse, the signal to be processed will normally be the second half of a spin echo. In the analysis presented here, it will be assumed that the second half of the echo has the same shape as the FID. It will also be assumed that the effect of the pulsed rf field is that same for all parts of the NMR line as it would be for a line that is a broad superposition of narrow, purely magnetic spin packets.

Another important assumption of our analysis is that, except for the nonlinear operation of applying rf pulses to nuclear spins, the response of the spins and the apparatus are linear. This assumption is important for applying the Fourier analysis to the problem and, for practical reasons, to permit linear averaging of the signal when the signal-to-noise ratio is poor. It will also be assumed that the field sweep does not change the shape of the NMR spectrum.

Because of the complications introduced by the factors $G(\bar{\gamma}\Delta B_n + f_k)$ and $M(\bar{\gamma}\Delta B_n + f_k)$, which often are not known or easily modeled, it is necessary to introduce additional measurement and processing steps to obtain the NMR spectrum $P(f_k)$. The key steps of the FSS method are to (1) to record a series of signals $r_n(t)$ in the time domain using different values of ΔB_n , (2) shift the frequency of each of them by $\bar{\gamma}\Delta B_n$ with numerical processing, and (3) sum the result. The requirements on the spacing and range of ΔB_n to obtain a good measurement of $P(f_k)$ are discussed in Sec. IV A.

The detected signal of the k th isochromat is given by Eq. (9). Shifting its frequency by $-\bar{\gamma}\Delta B_n$ corresponds to multiplication of the signal in the time domain by $\exp(-i2\pi\bar{\gamma}\Delta B_n t)$ [Eq. (4)] to give

$$r_n(f_k, t) e^{-i2\pi\bar{\gamma}\Delta B_n t} = P(f_k) G(\bar{\gamma}\Delta B_n + f_k) \times M(\bar{\gamma}\Delta B_n + f_k) e^{i2\pi(f_0 + f_k)t}. \quad (16)$$

The right-hand side of Eq. (13) corresponds to the spectral density $P(f_k) G(\bar{\gamma}\Delta B_n + f_k) \times M(\bar{\gamma}\Delta B_n + f_k)$ located at $f_0 + f_k$. Next, the sequence of frequency shifted signals is summed, which gives

$$\begin{aligned}
r(f_k, t) &= \sum_n r_n(f_k, t) e^{-i2\pi\tilde{\gamma}\Delta B_n t} \\
&= \sum_n P(f_k) G(\tilde{\gamma}\Delta B_n + f_k) M(\tilde{\gamma}\Delta B_n + f_k) e^{i2\pi(f_0 + f_k)t} \\
&= P(f_k) e^{i2\pi(f_0 + f_k)t} \\
&\quad \times \left[\sum_n G(\tilde{\gamma}\Delta B_n + f_k) M(\tilde{\gamma}\Delta B_n + f_k) \right] \\
&= Q(f_k) P(f_k) e^{i(2\pi f_0 + f_k)t}, \tag{17}
\end{aligned}$$

where

$$Q(f_k) = \sum_n G(\tilde{\gamma}\Delta B_n + f_k) M(\tilde{\gamma}\Delta B_n + f_k). \tag{18}$$

The function $Q(f_k)$ samples the product $G(\tilde{\gamma}\Delta B_n + f_k) M(\tilde{\gamma}\Delta B_n + f_k)$ at the discrete points $\tilde{\gamma}\Delta B_n + f_k$ and sums these values.

Finally, this response for each isochromat is integrated over the NMR frequency to obtain the FSS transient signal $r(t)$:

$$\begin{aligned}
r(t) &= \int_{-\infty}^{\infty} r(f_k, t) df_k \\
&= e^{i2\pi f_0 t} \int_{-\infty}^{\infty} Q(f_k) P(f_k) e^{i2\pi f_k t} df_k. \tag{19}
\end{aligned}$$

We then stipulate that the points ΔB_n over which the spectrum is summed are chosen to make Q independent of f_k . (How to satisfy this condition is discussed in the next section.) Under these circumstances,

$$r(t) = Q e^{i2\pi f_0 t} \int_{-\infty}^{\infty} P(f_k) e^{i2\pi f_k t} df_k, \tag{20}$$

or

$$r(t) e^{-i2\pi f_0 t} \Leftrightarrow Q P(f). \tag{21}$$

Equation (21) is the main result of this paper. It shows that the Fourier transform of the frequency shifted, field swept FID or half echo is the NMR absorption spectrum. The aberrations associated with a B_1 too small to “cover” the NMR line and the frequency response of the receiver and NMR coil circuit are corrected, and the largest available B_1 can be used for maximum sensitivity.

In pulsed NMR spectroscopy B_1 usually varies over the sample volume. It is easily shown that as long as the NMR absorption spectrum is the same for each volume element, the above result can be averaged over the sample volume to give the same result. In this case, the product GM is understood to be this volume average.

Although the analysis presented here treats the various functions as continuous in time and frequency, the implementation of the algorithm will normally be done digitally with sampled waveforms and discrete Fourier transforms.⁷ When using these discrete variable transforms with the algorithm, it is essential to respect the Nyquist criterion for both

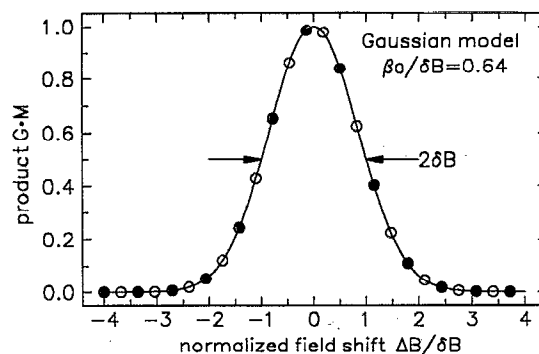


FIG. 3. Schematic representation of the sampled points of the product $G(\tilde{\gamma}\Delta B)M(\tilde{\gamma}\Delta B)$ as a function of the normalized field shift for each step used with the field-stepped FSS method. The solid curve corresponds to a Gaussian for GM with a full width at half maximum equal to $2\delta B$, which is close to $2B_1$ (see Fig. 7). The solid circles show the sample points for one value of f_k and the open ones for another.

the original waveforms and the processed ones, i.e., the discrete waveform in the time domain must include at least two points for the highest frequency present in the waveform.

The algorithm and analysis presented here for the FSS method is expressed in terms of the frequency shift operation in the time domain. It can, of course, be applied as well in the frequency domain by Fourier transforming each $r_n(t)$, shifting the result by the corresponding frequency difference, and summing the result in the frequency domain. We prefer to execute the frequency shift in the time domain because there the shift $\tilde{\gamma}\Delta B_n$ can be applied over a continuous range whereas, in the frequency domain, the corresponding variable is discrete.

The emphasis in this paper has been the NMR absorption, i.e., the imaginary part of the transverse nuclear susceptibility. When both in-phase and quadrature detection are employed for $r(t)$, the corresponding Fourier transform also includes the dispersion, or the real part of the transverse nuclear susceptibility. The analysis presented in this paper applies to the dispersion as well as to the absorption signal.

A. Spectrum sampling requirements

The condition that determines the required values for ΔB_n is that $Q(f_k)$ [Eq. (18)] should be independent of f_k within the accuracy needed for the NMR spectrum. There are two conditions to be met: the width of the steps $\Delta B_n - \Delta B_{n-1} = \beta_n$ and the total range of the magnetic-field sweep. For the isochromat at f_k , Q_k is a sample over the product $G(\tilde{\gamma}\Delta B_n + f_k) M(\tilde{\gamma}\Delta B_n + f_k)$. These sampling points are shown schematically by the solid circles on Fig. 3 and by the open circles for a different value of f_k .

Qualitatively, it is evident that the sum of the sampled points will be the same for any two values of f_k as long as (1) the sampling points ΔB_n cover the range where $G(\tilde{\gamma}\Delta B_n + f_k) M(\tilde{\gamma}\Delta B_n + f_k)$ has significant values and (2) the step width is small compared to any range of $\tilde{\gamma}\Delta B_n + f_k$ over which $G(\tilde{\gamma}\Delta B_n + f_k) M(\tilde{\gamma}\Delta B_n + f_k)$ changes significantly. The condition that Q be independent of f_k also requires that the field sweep range brings the entire NMR spec-

trum across the range where $G(\gamma\Delta B_n + f_k)M(\gamma\Delta B_n + f_k)$ differs significantly from zero. Thus the required frequency range of the field sweep extends from the full range of significant values of $G(\gamma\Delta B_n + f_k)M(\gamma\Delta B_n + f_k)$ below the NMR spectrum to the same extent above it.

Now we present a numerical simulation example to show the effect of the step width and the sweep range on the accuracy of the spectral reconstruction when the Fourier transform is obtained from a spin echo. The product $G(\gamma\Delta B_n + f_k)M(\gamma\Delta B_n + f_k)$ will be modeled by a function whose width is determined mainly by the smaller of the two. For G , this width is the bandpass of the receiver. The width of M depends on the bandwidth of the NMR coil system and the value of B_1 . For our example we will assume the width of the product GM is limited mainly by M and that the product is a Gaussian of the form

$$G(\gamma\Delta B)M(\gamma\Delta B) = \exp\left[-0.693\left(\frac{\Delta B}{\delta B}\right)^2\right], \quad (22)$$

where $2\delta B$ is the full width at half maximum. This function is shown by the solid line in Fig. 3. Equal field step widths $\beta_n = \beta_0$ will be used, although that is not necessary. (We expect that the most efficient application of the FSS method will use *unequal* step widths.)

First, consider the error associated with the step size for a sweep range that is small enough that it does not introduce any error into the evaluation of $Q(f_k)$. A given isochromat will sample $G(\gamma\Delta B)M(\gamma\Delta B)$ at a series of points shown, for example, by the filled circles in Fig. 3. Only the sampling points shown will contribute significantly to $Q(f_k)$ because $G(\gamma\Delta B)M(\gamma\Delta B)$ is negligible beyond $\beta_0/\delta B \approx \pm 2$.

For equally spaced field sampling points, Q for any isochromat is a periodic function of its position between two adjacent sampling points (adjacent solid circles on Fig. 3). It is therefore sufficient to evaluate the error associated with the finite field step width by calculating Q at a series of f_k values that span one field step. We use the corresponding fractional rms variation of Q over one interval as the measure of the error ($\delta Q_{\text{rms}}/\langle Q \rangle$) induced by the finite size of the field step:

$$\frac{\delta Q_{\text{rms}}}{\langle Q \rangle} = \frac{1}{\langle Q \rangle} \sqrt{\frac{1}{N} \sum_{f_k=f_k}^{f_k+\gamma\beta_0} [Q(f_k) - \langle Q \rangle]^2}, \quad (23)$$

where $\langle Q \rangle$ is the average value of Q over the interval of the summation and N is the number of isochromats in the sum.

Figure 4(a) shows the variation of $\delta Q_{\text{rms}}/\langle Q \rangle$ with the normalized step size $\beta_0/\delta B$ for the Gaussian model shown in Fig. 3. The error associated with the finite field step width drops rapidly for $\beta_0/\delta B < 1.5$, where the rms error is about 4%, and it is less than 1% for $\beta_0/\delta B < 1.3$. The calculated effect of the step size on the model spectrum of Fig. 2 is shown in Fig. 4(b) for the same Gaussian model. The heavy solid line is the model spectrum and the dotted and dashed lines are the spectrum obtained with the FSS algorithm for the ratios $\beta_0/\delta B$ indicated on the figure. There, it is seen that for $\beta_0/\delta B = 1.56$ (light solid line), the distortion of the spectrum is almost invisible on the figure. On the other hand, $\beta_0/\delta B \geq 2$ leads to a substantial distortion of the model spec-

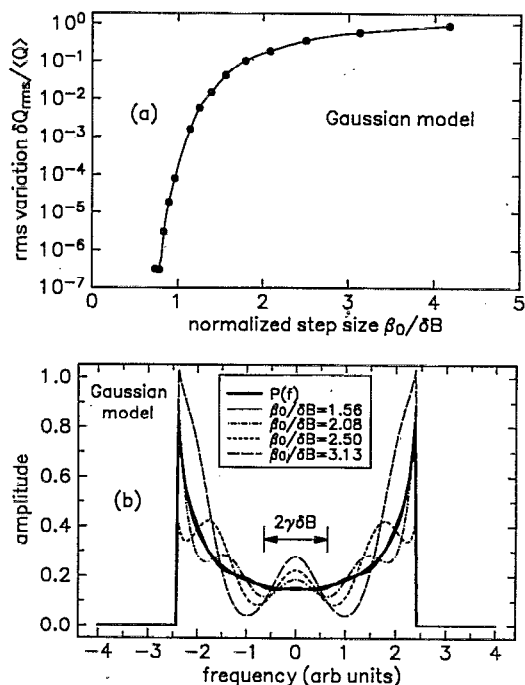


FIG. 4. (a) Normalized rms variation of the sum Q [Eq. (15)] as a function of the normalized field step size for the Gaussian model of Fig. 3. The variation of Q drops rapidly to a very small value when the step size is decreased to near the half width of $G(\gamma\Delta B)M(\gamma\Delta B)$. (b) Spectra of Fig. 2 obtained with the FSS algorithm for different field step widths using the Gaussian model of Fig. 3. The distortion for $\beta_0/\delta B = 1.56$ is barely visible, but it becomes severe for $\beta_0/\delta B \geq 2$.

trum. This graph illustrates the extreme rapidity of the onset of distortion with step width shown in Fig. 4(a). Even though the error evaluated here applies strictly only to the Gaussian model, it gives a good, semiquantitative guide for the practical application of the method.

The effect on Q of truncating the range of the field sampling points is easily evaluated for one isochromat by using closely spaced field steps and calculating Q for a set of points whose lowest field value ΔB_{min} starts well below the center of the system response ($\Delta B_{\text{min}}/\delta B < -3$) and terminating the sweep at ΔB_{max} near the center of the response. The effect of this sweep truncation on Q for a single isochromat is shown for the Gaussian model in Fig. 5, where the fractional error in Q associated with truncating the sweep is plotted as a function of $\Delta B_{\text{max}}/\delta B$. There it is seen that the sweep truncation error is less than 1% as long as ΔB_{max} for the corresponding isochromat extends beyond $+2\delta B$. Thus if each isochromat is swept through the range $\pm 2\delta B$, an accurate measurement of the NMR spectrum is obtained. For the full spectrum, this condition then requires that the field sweep extend $\pm 2\delta B$ beyond the extremities of the spectrum. Any part of the spectrum that is not swept fully through the system response will have its amplitude correspondingly changed by the reduction in Q . Although this example applies strictly only to the Gaussian model, it provides a sound, semiquantitative estimate of the consequences of truncating the range of the field sweep.

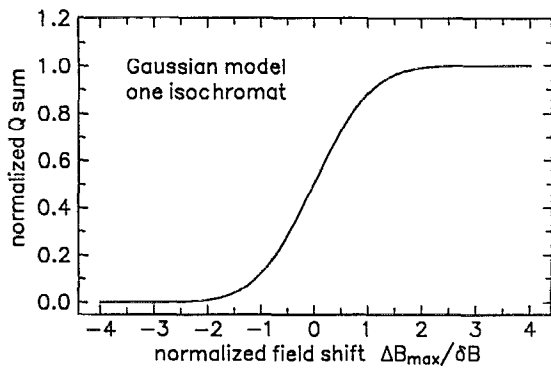


FIG. 5. Error for a one isochromat in comparison to the nontruncated case when the range of the field sweep is reduced to exclude traversing part of the product $G(\tilde{\gamma}\Delta B)M(\tilde{\gamma}\Delta B)$ for the Gaussian model. The corresponding error is less than 1% when the part of the relative field shift that is not traversed exceeds 2.

B. Field shift accuracy requirement

Application of the FSS algorithm requires an operation with the individual field steps ΔB_n . There will always be some error in the values assigned to them, with a corresponding error in the reconstruction of the spectrum. Here we briefly discuss the consequences of this error.

For each $\tilde{\gamma}\Delta B_n$, assume an error $\tilde{\gamma}b_n$ in the frequency shift $\tilde{\gamma}B_n + \tilde{\gamma}b_n$ used for the FSS algorithm. For a small, random error, this situation can be thought of as a small variation of the magnetic field from what it should be for each measurement. The effect on a single isochromat is that successive measurements will be shifted in field (or frequency) by a small amount, with the qualitative result that with spectral reconstruction the isochromat is broadened by the width of the distribution of b . Thus the effect on the full reconstructed NMR spectrum is qualitatively similar to convoluting it with another line whose shape is the distribution of b . It then follows that the width of the distribution of b should be small compared to any feature of the NMR line shape that is to be resolved. For a broad, relatively featureless line shape, the requirement for the accuracy of $\tilde{\gamma}\Delta B_n$ is rather loose. For a line with sharp features, such as narrow peaks or discontinuities, this requirement can be severe.

For a quantitative treatment of this situation, Eq. (16) can be written as

$$\begin{aligned} r_n(f_k, t) e^{-i2\pi\tilde{\gamma}\Delta B_n t} e^{i\tilde{\gamma}b_n} \\ = P(f_k + \tilde{\gamma}b_n) G(\tilde{\gamma}\Delta B_n + f_k + \tilde{\gamma}b_n) \\ \times M(\tilde{\gamma}\Delta B_n + f_k + \tilde{\gamma}b_n) e^{i2\pi(f_0 + f_k)t}, \end{aligned} \quad (24)$$

where the effect of $\tilde{\gamma}b_n$ has been placed into the arguments of P , G , and M using Eq. (4). As long as $\tilde{\gamma}b_n$ is very small compared to the width of the product GM , which will normally be the case, to a good approximation the term $\tilde{\gamma}b_n$ can be dropped from their arguments to obtain

$$\begin{aligned} r_n(f_k, t) e^{-i2\pi\tilde{\gamma}\Delta B_n t} e^{i\tilde{\gamma}b_n} \\ \simeq P(f_k + \tilde{\gamma}b_n) G(\tilde{\gamma}\Delta B_n + f_k) \\ \times M(\tilde{\gamma}\Delta B_n + f_k) e^{i2\pi(f_0 + f_k)t}, \end{aligned} \quad (25)$$

which corresponds to a small shift of the NMR spectrum for successive steps in the spectral reconstruction. A general, quantitative evaluation of the effect requires that Eq. (25) be known for the particular circumstances. The result will depend on whether the errors are systematic or random, etc. A particularly simple case occurs when the signal is averaged a large number of times (m) at each ΔB_n and there is a random change in the magnetic field for each measurement (b_m) with the same distribution $\rho(\tilde{\gamma}b)$ for each n . Then Eq. (20) becomes

$$r(t) \simeq Q e^{i2\pi f_0 t} \int_{-\infty}^{\infty} \bar{P}(f_k) e^{i2\pi f_k t} df_k, \quad (26)$$

where

$$\bar{P}(f_k) = \frac{1}{M} \sum_{m=1}^M P(f_k + \tilde{\gamma}b_m) \simeq P(f_k) * \rho(f_k). \quad (27)$$

Equation (27) shows that for this case the effect of a random variation in magnetic field (or the error in the field shift used to calculate the FSS spectral reconstruction) is to replace each impulse function isochromat by a distribution of frequencies whose shape is $\rho(f)$. Since it occurs for each isochromat, the reconstructed spectrum is the convolution $P(f_k) * \rho(f_k)$, as indicated in the qualitative discussion at the beginning of this section.

There is an effective strategy that can sometimes be used to help determine the field at each step for reconstructing the spectrum. It is to add one or more sharp field marker signals to the sample and to use the frequency of their NMR signal to determine the frequency shift to be used with Eq. (16).

C. System response measurement

To choose appropriate values of ΔB_n by applying the ideas of Sec. IV A requires knowing at least approximately the width and shape of the product $G(\tilde{\gamma}\Delta B)M(\tilde{\gamma}\Delta B)$. This product can, in principle, be calculated from a detailed knowledge of the instrumentation. It is, however, usually more practical to measure it, or simply to have an approximate understanding of its width and use a field step width conservatively chosen to be small enough to insure that the distortion of the spectrum introduced by it does not exceed an acceptable level. In this section, we describe several ways to measure the system response or, alternatively, to evaluate the distortion of the MR spectrum caused by the field step width.

The width of $G(\tilde{\gamma}\Delta B)$ is easily obtained by measuring the electrical response of the MR receiving system. For spin echoes, there is the rough rule of thumb that the width of M is approximately $\tilde{\gamma}B_1$ as long as the magnetic induction circuit has a bandwidth that is at least somewhat broader than $\tilde{\gamma}B_1$. One of the major advantages of the FSS method is that as long as the step size β_n is somewhat smaller than the width of $G(\tilde{\gamma}\Delta B)M(\tilde{\gamma}\Delta B)$, an accurate knowledge of it is not needed. There are, however, situations where it is important to know the form of $G(\tilde{\gamma}\Delta B)M(\tilde{\gamma}\Delta B)$ to make the best use of the FSS method. In this section we describe two experimental methods for obtaining an experimental measure-

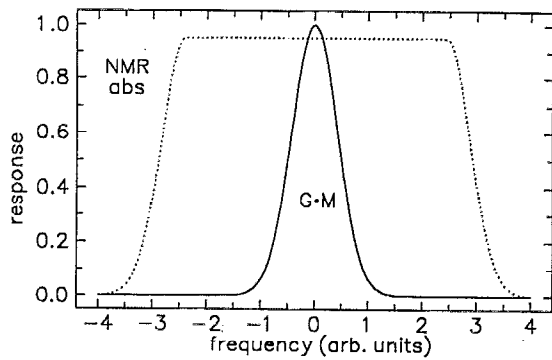


FIG. 6. Schematic representation of the MR absorption line shape (dotted curve) and the product $G(\bar{\gamma}\Delta B)M(\bar{\gamma}\Delta B)$ (solid curve) for an inhomogeneously broadened line whose absorption is flat in the region where GM differs significantly from zero. The Fourier transform of the corresponding spin echo is proportional to $G(f)M(f)$.

ment of $G(\bar{\gamma}\Delta B)M(\bar{\gamma}\Delta B)$. They will be discussed for application of the FSS method to spin echo measurements because that is usually the most viable kind of spectral measurement for NMR lines that have severe inhomogeneous broadening.

The first method is simply to measure the amplitude of the spin echo of a very narrow line as it is field swept through the response of the spectrometer. In this case we use $P(f_k) = \delta(f_k)$ in Eq. (10) to obtain

$$r_n(t) = e^{i2\pi(f_0 + \bar{\gamma}\Delta B_n)t} G(-\bar{\gamma}\Delta B_n)M(-\bar{\gamma}\Delta B_n). \quad (28)$$

Equation (28) shows that the height of the spin echo (or the FID at $t=0$) at each point is simply a sample of $G(\bar{\gamma}\Delta B)M(\bar{\gamma}\Delta B)$ at each corresponding frequency from resonance. An example of such a measurement is discussed in Sec. V.

The second method is to calculate at a single value of the magnetic field the Fourier transform of the echo of an NMR line that is so broad that it is essentially flat all the way across the region for which $G(-\bar{\gamma}\Delta B)M(-\bar{\gamma}\Delta B)$ has significant values. Such a line shape can often be formed, for example, by placing the sample in a large magnetic field gradient along its length. [In this case, B_1 should be uniform enough over the sample to avoid significant correlation between the spectral frequency and B_1 —see the comment on spatial averaging following Eq. (21).] A cartoon of an extreme example is shown in Fig. 6 (an NMR spectrum flat over ± 1 frequency units would be sufficient). In this case, integrating $r(f_k, t)$ over f_k [Eq. (10)] gives

$$\begin{aligned} r(t) &= \int_{-\infty}^{\infty} r(f_k, t) df_k \\ &= e^{i2\pi f_0 t} P(0) \int_{-\infty}^{\infty} G(f_k)M(f_k) e^{i2\pi f_k t} df_k, \end{aligned} \quad (29)$$

where $P(f_k)$ has been taken out of the integral because it is a constant where the integrand is not zero and we have set $\bar{\gamma}\Delta B_n = 0$. Equation (29) shows that, in this case, $r(t) \Leftrightarrow G(f)M(f)$.

With these two methods, it is possible to obtain the shape of $G(\bar{\gamma}\Delta B)M(\bar{\gamma}\Delta B)$ from spin echo measurements.

The field sweep measurement for a very narrow line can also be used to obtain the product GM for FID signals. In this case, the narrow line is swept through the spectrometer response range. The initial value of the FID gives the product GM . The behavior of M is much more complex for this case. In particular, it has oscillations and a substantial imaginary component.⁵ Since the initial part of the FID is usually not accessible for strongly inhomogeneously lines, we do not discuss this case further.

Finally, we point out another strategy to estimate the largest permissible step width β_n when the FSS processed spectrum has a large S/N and the values of β_n are small compared to the width of GM . It is to process the spectrum using the FSS algorithm with subsets of the data corresponding to progressively wider field steps. As long as the field steps are close enough together, the same spectrum will be obtained. When, however, the field steps used for the analysis are too large, there will be a corresponding change in the spectrum that shows the maximum step size β_{\max} that can be used to obtain a spectrum with a small distortion. The discussion of Sec. IV A shows that the rms distortion is about 10% for $\beta_{\max} \sim 1.8 \gamma \delta B$.

D. Sensitivity considerations

In this section we present a brief, semiquantitative comparison of the FSS method with the SEHS scheme. It will be assumed that the same spectrometer and sample are used so that these factors do not enter. Furthermore, it will be assumed that receiver noise is independent of frequency (“white”) and that equally spaced steps and a constant B_1 for the field sweep are used for each method. We will also assume that a wide, inhomogeneously broadened line is under study and that the spin echo measurement destroys the relevant longitudinal magnetization so that the same recovery time and repetition rate for measurements applies to both methods. It will also be assumed that the width of M is dominated by B_1 , i.e., the bandwidth of the receiver coil circuit is substantially larger than $\bar{\gamma}B_1$.

Let the overall frequency width of the NMR line be W and the width of the smallest feature to be measured be w . The signal-to-noise ratio (S/N) on a single measurement is proportional to the number of precessing spins and inversely proportional to the square root of the bandwidth (f_R) of the receiving system. The minimum value of f_R that can be used is the inverse of the characteristic duration of the echo, or $f_R \approx \bar{\gamma}B_1$. The number of precessing spins is proportional to B_1 .

Thus for a single echo the signal voltage S is proportional to $\bar{\gamma}B_1$ and the noise voltage N is proportional to $\sqrt{f_R} \sim \sqrt{\bar{\gamma}B_1}$, so that $S/N \propto \sqrt{\bar{\gamma}B_1}$. With the FSS scheme, one uses the maximum value of B_1 available ($B_{1\max}$) to obtain $S/N \propto \sqrt{\bar{\gamma}B_{1\max}}$. For the SEHS method, a measurement that yields five independent, sampled points over w implies $\bar{\gamma}B_1 \sim 0.25w$, which corresponds to $S/N \propto \sqrt{0.1w}$. The ratio of S/N for the two cases is then

$$\frac{(S/N)_{\text{FSS}}}{(S/N)_{\text{cSES}}} \approx \sqrt{\frac{\bar{\gamma}B_{1\max}}{0.1w}}. \quad (30)$$

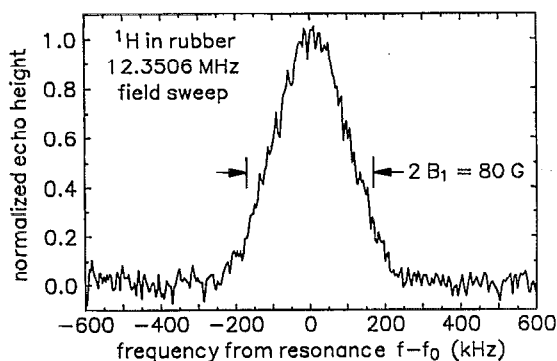


FIG. 7. Measured height of the spin echo signal from the narrow proton NMR signal in rubber as a function of the frequency from resonance. The experimental curve is a measurement of the shape of $G(f)M(f)$ using Eq. (25). Comparison with Fig. 3 shows that its shape is close to Gaussian and that δB is approximately B_1 .

If the spectrum has a feature for which $w \sim 0.1 \gamma B_{1\max}$, one obtains an S/N that is approximately a factor of 10 in favor of the FSS method. The corresponding reduction in averaging time for the same S/N is 100 times. In addition to this increased efficiency of accumulation, one obtains a more accurate representation of sharp spectral features with the FSS method.

There is another advantage of the FSS method when the signal is large enough that averaging is not necessary to obtain an adequate S/N. In this case, the time needed to record the entire spectrum is proportional to the number of field steps needed to cover all of it. If the rather conservative field step spacing $1.0 B_{1\max}$ is chosen for the FSS measurement, approximately $W/\gamma B_{1\max} + 4$ steps are needed. For a broad spectrum with $W/\gamma B_{1\max} = 6$, the FSS measurement then takes ten steps. For the SEHS method, if $W = 10w$ and five points are sampled across w , 50 steps are needed, i.e., $5 \times$ that of the FSS measurement. In addition to the significant reduction in measurement time for the FSS method for this example, one benefits from its increased S/N and superior spectral resolution.

The SEIS method lies between the SEHS and FSS methods in terms of the sensitivity considerations just discussed. Here we indicate qualitatively the relation of the SEIS method to them. Like the FSS method, it permits using a large B_1 to obtain a large signal amplitude. On the other hand, it is a point measurement in the frequency domain, so that a large number of points must be recorded to measure a spectrum with many details. If, as can easily be shown, the S/N is enhanced by integrating only part of the signal, there is a corresponding decrease in the spectral resolution associated with each measurement.

VI. STEPPED-FIELD EXAMPLE

Here we present measurements of the system response and a comparison of an NMR spectrum obtained by the FSS and SEHS methods as a demonstration of the utility of the FSS method. First, we show the system response obtained by sweeping a narrow line through resonance and recording the height of the spin echo signal [Eq. (28)]. Figure 7 shows

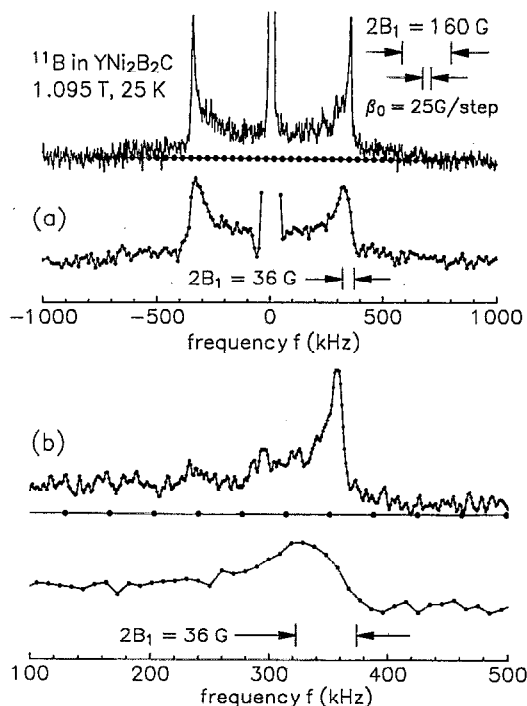


FIG. 8. Field-stepped FSS (upper curve, $2B_1 = 160$ G) and SEHS (lower curve, $2B_1 = 36$ G) recordings of the ^{11}B NMR absorption signal in $\text{YNi}_2\text{B}_2\text{C}$: (a) full spectrum, (b) enlarged region. The large dots below the upper curve on each plot identify the points at which spectra were recorded for the FSS processing using a fixed step width $\beta_0 = 25$ G. The same repetition rate was used for both curves and the total accumulation time for the lower curve is twice that of the upper one. The signal-to-noise ratio for the broad parts of the upper curve (including further smoothing) relative to the lower one is approximately 1.5:1, and a much better resolution of the discontinuities in the spectrum is obtained. The smearing of the discontinuities with the SEHS method is approximately $2B_1$, as expected.

such a signal using the proton signal from rubber, whose width is much less than γB_1 , as a function of the frequency from resonance. The recorded echo height is proportional to the response of the system, i.e., to the product GM . As conjectured earlier in this paper, the FWHM width of the response is close to $2B_1$. By inspection, it is also seen that the form of the curve is close to the Gaussian model that was used for Fig. 3. Measurements of the kind shown in Fig. 7 are easy to make; they are an effective way to obtain the system response for evaluating the most efficient way to use the FSS method.

A comparison of the FSS and the SEHS methods is shown in Fig. 8, where the spectrum of ^{11}B in $\text{YNi}_2\text{B}_2\text{C}$ is shown at 25 K in an applied field of 1.095 T. The upper pair of curves (a) are the full spectrum and the lower two (b) are an expanded view of one part of it. The large, inhomogeneous broadening is the powder pattern of the ^{11}B nuclei in an axially symmetric field gradient.¹⁴ It has a narrow central transition (truncated in the figure) broadened by the second order quadrupolar interaction and two, equally spaced first order quadrupolar interaction discontinuities about 0.05 T apart. Dipolar broadening causes an additional convolution in the frequency domain with a roughly Gaussian line with an rms half width of about 2 kHz. A single quadrupolar interaction frequency gives an excellent fit to all of the features of the line.¹⁴

The upper curve is the spectrum obtained with the field-stepped FSS method using $B_1=80$ G, which is then approximately the half width of the system response. The large, filled circles along the baseline show the actual acquisition points. They are 25 G apart, which corresponds to $\beta_0/\delta B \approx 0.3$. This value is well within the guidelines of Sec. IV A to obtain an accurate measurement of the spectrum. The repetition time of the measurements was long enough (1.5 s) to insure recovery of the nuclear magnetization between measurements.

A measurement of the same spectrum using the SEHS method is shown in the lower curve. The same pulse repetition rate was used, but B_1 was reduced to 18 G to obtain a reasonable spectral resolution. For the part of the curves shown, a total of twice as many pulses were recorded for the lower curve (twice the acquisition time). From the analysis of Sec. IV A, it is expected that S/N for the FSS method relative to the SEHS measurement should be approximately $\sqrt{B_{1\text{FSS}}/B_{1\text{cSES}}} \approx 2.1 \times$ the square root of the ratio of the number of acquisition pulses, which applies an additional factor $1/\sqrt{2}$, for an overall S/N of 1.5 in favor of the FSS method for half the acquisition time. This value is close to the observed S/N ratio of the broad parts of the line when additional smoothing is done. The improvement in the S/N ratio is even larger when the sharp features of the spectrum are considered and, of course, the FSS method gives a much more faithful rendition of the sharp features of the spectrum. It is also evident that the magnitude of the smearing of the spectral discontinuity that occurs with the SEHS method is about $2B_1$, as expected.

VII. FREQUENCY-STEPPED FSS SPECTROSCOPY

Two situations in which it is not possible to use the field-stepped FSS method are pulsed NMR spectroscopy with a magnetic field which is impractical or impossible to sweep (often the case with contemporary superconducting magnets) and pulsed pure NQR spectroscopy. For these cases, it can be advantageous to use a swept-frequency variant of the FSS method. Here we discuss briefly the main considerations for its application using pure NQR in zero magnetic field as the example.

The NQR spectrum is determined by the tensor interaction of the electric field gradient at the nucleus and the nuclear quadrupole moment.¹⁵ If the sample is a perfect crystal, there will normally be a finite number of discrete spectral lines which, if sufficiently separated in frequency, can be thought of as an inhomogeneously broadened spectrum that has a limited number of isochromats. For a variety of reasons, one often finds an inhomogeneously broadened spectrum caused by a distribution of electric field gradients. The usual reasons for this distribution are a structural superstructure (commensurate or incommensurate), imperfections in the sample (dislocations, grain boundaries, interstitial ions, vacancies, atomic substitutions, etc.), or the structure of the sample itself (random alloy or disordered solid). Regardless of the origin of the inhomogeneous broadening, the FSS method can be used when the spectrum is well represented by a superposition of isochromats.

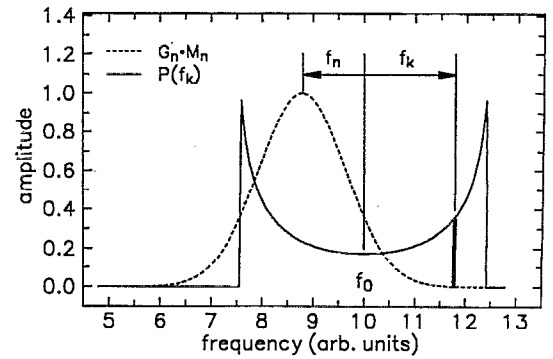


FIG. 9. Schematic representation of the frequency-stepped MR/NQR responses. The solid line is the MR/NQR absorption spectrum $P(f)$ and the heavy vertical line is one isochromat shifted by the frequency f_k from the fixed point f_0 . The dashed line is proportional to the real part of the product $G(f)M(f)$, which is stepped past $P(f)$ by changing the spectrometer frequency.

The analysis used for the application of the FSS method to NQR spectroscopy follows closely that of the MR case. There are two main differences: (1) Because there is no magnetic field sweep, the frequency of the spectrometer must be swept to traverse the spectrum, with the consequence that there may be a significant change in the electrical response of the magnetic induction circuit and the receiving system to different parts of the spectrum, (2) the value of B_1 may change with the frequency, and (3) for NQR, the response of the spins to B_1 changes according to the transition that is excited and to the orientation of the principal axes of the electric field gradient tensor relative to the direction of B_1 . The effect of these differences is modeled by functions G and M that vary across the spectrum. An important practical complication is that a broad frequency sweep is usually more difficult to implement than a field sweep when readjustment of the magnetic induction circuit is required.

Figure 9 shows the relationship of the quantities used to analyze the application of the frequency-stepped FSS method to pulsed NQR spectroscopy. A model of the absorption amplitude of the NQR spectrum is represented by a superposition of isochromats at fixed frequencies f_k relative to a point on the spectrum at f_0 with the distribution $P(f_k)$ (solid line). As before, the combined response of the nuclear spins and the magnetic induction circuit are represented by the function $M_n(f-f_n)$ and the gain of the receiving system by $G_n(f-f_n)$, where f_n is the displacement of the n th acquisition frequency relative to f_0 . The subscript n on G and M signifies that in general these functions vary with the acquisition frequency. An FSS measurement sequence corresponds to stepping the product $G_n(f-f_n)M_n(f-f_n)$ (dashed line on Fig. 9) past $P(f_k)$.

The frequency-stepped FSS processing procedure analogous to that used for the field-stepped case includes the following steps. The detected signal of the k th isochromat is shifted by f_n to give

$$r_n(f_k, t) e^{-i2\pi f_n t} = P(f_k) G_n(f_n + f_k) \times M_n(f_n + f_k) e^{i2\pi(f_0 + f_k)t}. \quad (31)$$

Then, the sequence of frequency shifted signals is summed to yield

$$\begin{aligned}
 r(f_k, t) &= \sum_n r_n(f_k, t) e^{-i2\pi f_n t} \\
 &= \sum_n P(f_k) G_n(f_n + f_k) M_n(f_n + f_k) e^{i2\pi(f_0 + f_k)t} \\
 &= P(f_k) e^{i2\pi(f_0 + f_k)t} \left[\sum_n G_n(f_n + f_k) M_n(f_n + f_k) \right] \\
 &= V(f_k) P(f_k) e^{i(2\pi f_0 + f_k)t}, \tag{32}
 \end{aligned}$$

where, for the frequency-stepped case,

$$V(f_k) = \sum_n G_n(f_n + f_k) M_n(f_n + f_k). \tag{33}$$

By integrating this response for each isochromat over the NQR frequency we obtain the FSS transient signal $r(t)$:

$$\begin{aligned}
 r(t) &= \int_{-\infty}^{\infty} r(f_k, t) df_k \\
 &= e^{i2\pi f_0 t} \int_{-\infty}^{\infty} V(f_k) P(f_k) e^{i2\pi f_k t} df_k. \tag{34}
 \end{aligned}$$

Two main differences arise in comparison with the field-stepped case. The first is that because of the change in frequency, there is a fundamental change in the amplitude of the signal generated by the spins in a given isochromat. It is proportional to the square of the spectrometer frequency (one power for the high temperature Boltzmann population factor and one for the amplitude of the emf induced by each precessing spin). If the goal of the measurement is to obtain the number of spins in each isochromat, the signal should be normalized by the square of its frequency

The second one is, in contrast with the field-stepped method, the difficulty of making $V(f_k)$ independent of f_k . There appears to be no systematic way to do so. The consequence is that $r(t) \Leftrightarrow V(f_k)P(f_k)$ instead of $r(t) \Leftrightarrow P(f_k)$. There are, however, several strategies that can be employed to mitigate this situation. We now discuss some of their general features.

If the fortunate circumstance occurs that the dependence of $V(f_k)$ on f_k is weak because of the spectrometer design and/or a narrow frequency sweep range, it may be sufficient simply to approximate it as a constant to obtain $r(t) \Leftrightarrow P(f_k)$. It is not, unfortunately, straightforward to determine in practice how serious is this approximation.

When the dependence of $V(f_k)$ on f_k is not negligible, a general approach is to measure or model $V(f_k)$ and use it to correct the measured spectrum. However, care must be exercised in doing so. The correction is to multiply the measured $V(f_k)M(f_k)$ by a measured or calculated $1/V(f_k)$. To avoid a spurious correction in parts of the spectrum where $V(f_k)$ is small or uncertain, the frequency range of the correction must be limited to regions where $V(f_k)$ is relatively large and well known.

Several strategies can be implemented to measure the quantities that contribute to $V(f_k)$. It is relatively straightforward to measure the term $G(f)$, which represents the gain of the receiving system, by injecting a known signal into the input of the receiver and measuring its frequency response using the same conditions as for the spectrum measurement. In doing so, care must be taken to account for the frequency dependent phase shift associated with the various cable lengths.

Evaluating $M(f)$ is much less straightforward because it represents both the size of the excited precessing magnetization and the response of the magnetic induction circuit to it at the different frequencies of the spectrum. The amplitude of the response to a standard magnetic induction signal over a range of frequencies and tuning conditions can be measured by incorporating a broadband, weakly coupled mutual inductance (antenna) to the magnetic induction circuit and measuring the magnitude and phase of the induced signal. Such a mutual inductance can be implemented, for example, by a transmission line one end of which is terminated near the magnetic induction circuit by a small loop in series with its characteristic impedance. If the entire receiving system is used for this measurement, $G(f)$ can also be obtained. The practical implementation of this approach requires great care to insure that the antenna system has a response and a purely magnetic coupling whose variation is known or negligible over the frequency range of interest. Also, the proportionality of the induced voltage to the product of the coupled magnetic flux and the frequency must be accounted for to obtain the number of spins in each frequency range.

According to a reciprocity relation,¹⁶ the test signal induced into the magnetic induction circuit by the antenna can also be used to evaluate the change in B_1 with frequency. Once B_1 is known, it can be used for modeling its effect on the amplitude of the signal from the various parts of the spectrum. It often happens, however, that the parameters of this reciprocity relation during an rf pulse are different from what they are during reception of the small magnetic resonance signal because of the nonlinear, duplexing action of the spectrometer. In this case, B_1 can be scaled by using the antenna as the pickup element in a separate wideband receiving system that operates during the rf pulse.

In spite of the difficulties and uncertainties mentioned here, it is often possible to use the frequency-stepped FSS method to advantage in pulsed NQR and NMR spectroscopy. The main effect of the uncertainties is to give uneven weights over a broad frequency scale to different parts of the NQR spectrum. This circumstance can introduce an appreciable error in the assignment of the intensity to parts of the spectrum that are widely separated in frequency. On the other hand, the frequency and shape of narrow features are well represented. When the location of these features is the point of greatest interest in the spectrum, the frequency-stepped FSS method is particularly useful.

The criteria for the frequency step size and frequency sweep range are readily shown to be about the same as those developed for the NMR case (Sec. IV A) when the association $\tilde{\gamma}\Delta B_n \sim f_n$ is made, i.e., the frequency step size should be the lesser of $\tilde{\gamma}B_1$ or the bandwidth of the receiver, and the

range of the frequency sweep should go two of these steps beyond each part of the spectrum to be recorded. Also, the sensitivity gain relative to (swept frequency) SEHS is comparable to that discussed for the NMR case (Sec. IV D).

Three nice examples of NQR spectrum obtained with FSS processing have been reported by Ahrens *et al.*^{17,18} for the ¹³⁹La NQR signal in La₂CuO_{4+δ}. They show an excellent resolution of both narrow and broad features in the same spectrum. These spectra include a frequency correction obtained with a test signal that was inductively coupled into the sample coil using a small loop at the end of a cable terminated in its characteristic impedance.¹⁸

In summary, it is evident that the frequency-stepped FSS method can be used to advantage in NQR or fixed-field MR spectroscopy, but more work is needed to find ways to measure the relative intensity of features of the spectrum that are well separated in frequency.

VIII. CONCLUSIONS

We have presented and analyzed a novel method of Fourier transform processing for pulsed NMR and pulsed ESR spectroscopy of wide, inhomogeneously broadened lines. When the criteria for its application are met, it provides high resolution, high sensitivity, and it can remove the distortions introduced by the finite amplitude of the pulsed rf magnetic field and the finite bandwidth of all parts of the spectrometer. The method is to record the transient signal at a series of magnetic fields, then to process the transient signal by translating its frequency by the corresponding field shift for each point and summing the corresponding Fourier-transformed signals. Additional criteria for the range and step interval of the magnetic field variation are discussed. It is shown that in comparison with SEHS, a substantially improved sensitivity and spectral resolution can be obtained. The analog of the method for pulsed magnetic resonance and NQR spectroscopy that corresponds to sweeping the spectrometer frequency is also described. A semiquantitative discussion of this case shows that a good representation of the location and shape of sharp spectral features is obtained, that the sensitivity of the measurement is improved in comparison to SEHS, but that there may be significant uncertainties in the relative intensity of parts of the spectrum that are well separated in frequency.

Further work to be done on this subject is to evaluate it more quantitatively when the applicability criteria, such as strong inhomogeneous broadening, T_2 independent of spectral frequency, etc., are not met or when they are relaxed. Also, application of the analysis to the frequency-stepped case needs further development.

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¹By magnetic induction circuit we mean the structure into which the precessing magnetization induces an emf and the passive components to which it is connected. For a typical NMR spectrometer, it is the NMR coil and the associated cables, tuning, impedance matching, and duplexing components that comprise the NMR probe circuit. For a conventional microwave ESR spectrometer, it is the sample cavity and its coupling circuit.

²Although the cSES method has been used for a very long time, we do not know of an early, definitive discussion of its use. One of us (W. G. C.) has used it on occasion since about 1965. Two reports from the 1970s that use it are included below as Refs. 3 and 4. A text that mentions it is given in Ref. 5.

³D. Aliaga Guerra, P. Panissod, and J. Durand, *Solid State Commun.* **28**, 745, (1978).

⁴T. Kubo, K. Adachi, M. Mekata, and A. Hirai, *Solid State Commun.* **29**, 553 (1979).

⁵E. Fukushima and S. B. W. Roeder, *Experimental Pulse NMR: A Nuts and Bolts Approach* (Addison-Wesley, Reading, MA, 1981), p. 45.

⁶N. Winzek, F. Hentsch, M. Mehring, H. Mattausch, R. Kremer, and A. Simon, *Physica C* **168**, 327 (1990), state "The second half of the spin echo was Fourier transformed and different spectra for different frequency settings were overlaid.... By this technique we were able to obtain spin echo spectra which were not limited in resolution by pulse width or gating effects."

⁷E. O. Brigham, *The Fast Fourier Transform* (Prentice-Hall, Englewood Cliffs, NJ 1974).

⁸Since the units radians per second are usually used for γ in much of the NMR literature, we use the notation $\tilde{\gamma} = \gamma/2\pi$ when the intended units are MHz/T, as they are throughout this paper.

⁹Ref. 5, Sec. II A 2.

¹⁰W. G. Clark, *Rev. Sci. Instrum.* **35**, 316 (1964).

¹¹A. Avogadro, G. Bonera, and M. Villa, *J. Magn. Reson.* **35**, 387 (1979).

¹²B. Pedersen and W. G. Clark, *J. Chem. Phys.* **53**, 1024 (1970).

¹³If this condition is not satisfied because of a interference signals, a short T_2 , etc., the corresponding array can be constructed by catenating the second half of the echo with its time-reversed complex conjugate (mirror image).

¹⁴M. E. Hanson, F. Lefloch, W. H. Wong, W. G. Clark, M. D. Lan, C. C. Hoellwarth, P. Klavins, and R. N. Shelton, *Phys. Rev. B* (in press).

¹⁵C. P. Slichter, *Principles of Magnetic Resonance*, 3rd ed. (Springer, Berlin, 1990), Chap. 10.

¹⁶D. I. Hoult and R. E. Richards, *J. Magn. Reson.* **24**, 71 (1976).

¹⁷E. T. Ahrens, A. P. Reyes, P. C. Hammel, J. D. Thompson, P. C. Canfield, Z. Fisk, and J. E. Schirber, *Physica C* **212**, 317 (1993).

¹⁸E. T. Ahrens (unpublished).