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Time Saving in Measurement of NMR and EPR Relaxation Times*

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By producing a train of absorption or dispersion signals (continuous-wave magnetic resonance) or free induction decays (pulsed magnetic resonance) it is possible to save time in spin-lattice relaxation measurements due to the fact that it is not necessary to wait for equilibrium magnetization before initiating the train. The relaxation time may be calculated from the train according to a simple rapidly converging iteration.

INTRODUCTION

A PERIODIC train of magnetic field passages through resonance, or a periodic train of rf pulses at resonance produce, respectively, a corresponding train of absorption (or dispersion) signals or free induction decays, illustrated in Fig. 1; these may be analyzed to yield the spin-lattice relaxation time $T_1$.\(^1\) Methods and apparatus for accomplishing such experiments have been discussed for cw NMR,\(^1\)\(^2\) cw EPR,\(^3\) and pulsed NMR.\(^4\) It is the purpose of this paper to show that it is not necessary to wait for equilibrium of the spin system before initiating such a train of signals, and the resulting time saving may be considerable if $T_1$ is large.

I. THEORY

Following Look and Locker,\(^1\) let $\tau$ be the time between successive signals in the train and let $M_n^+$ and $M_n^-$ be, respectively, the magnetization along the magnetic field before and after the $n$th passage (or pulse). Furthermore, define the fraction of saturation, $X$, due to a passage (or pulse) by

$$M_n^+ = M_n^- (1-X), \quad 0 \leq X \leq 2,$$  

where $X=2$ would correspond to an adiabatic reversal or 180° pulse. Assuming that between successive passages $M$ relaxes exponentially we have

$$M_{n+1}^- = M_{eq}^- (1 - e^{-\tau/T_1}) + M_n^- e^{-\tau/T_1} = M_{eq}^- (1 - e^{-\tau/T_1}) + M_n^- (1 - X) e^{-\tau/T_1}, \quad (2)$$

where $M_{eq}^-$ is the equilibrium magnetization. Designating the first signal in the train as $M_0$ and letting $u = e^{-\tau/T_1}$ and $y= (1-X)$, we can relate $M_n$ to $M_0$ by induction, according to Eq. (2),

$$M_1^- = M_{eq}^- (1 - u) + M_0^- yu$$

$$M_2^- = M_{eq}^- (1 - u)[1 + yu] + M_0^- y^2 u^2$$

$$\vdots$$

$$M_n^- = M_{eq}^- (1 - u)[1 + yu + y^2 u^2 \cdots + y^{n-1} u^{n-1}] + M_0^- y^n u^n. \quad (3)$$

The observed signal $M_n$ will be proportional to $M_n^-$ so we can drop the superscripts and rewrite Eq. (3) as

$$M_n = M_{eq} (1 - u) \sum_{q=0}^{n-1} y^q u^q + M_0 y^n u^n$$

$$= M_{eq} (1 - u) \frac{1 - y^{n+1}}{1 - yu} + M_0 y^n u^n. \quad (4)$$

After many passages, the magnetization reaches a constant value $M_\infty$ given by Eq. (4) as

$$M_\infty = M_{eq} (1 - u) / (1 - yu) \quad (5)$$

and, thus,

$$(M_n - M_\infty) = (M_0 - M_\infty) [(1 - X) e^{-\tau/T_1}]^n, \quad (6)$$

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Fig. 1. A recorder tracing of a train of free induction decays in Mn\(^{2+}\)-doped H\(_2\)O, each decay following a pulse of about 48°. The time between pulses is $\tau$. For details of the calculation of $T_1$ see the text and Ref. 4.
or, using Eq. (5) to solve for \( X = 1 - \gamma \),
\[
(M_0 - M_{\infty}) = (M_0 - M_{eq}) \left[ \frac{e^{-T_1 \gamma}}{1 + \frac{M_{eq} - M_0}{M_0}} \right]^{n} e^{-T_1 \gamma} \left( M_M - M_{\infty} \right) \]
\[
-
\left[ \frac{M_{eq} - M_0}{M_0} \right]^{n} \right].
\tag{7}
\]

Taking logarithms of both sides gives an equation of the form \( Y = I + nS \) where \( I \) and \( S \) are, respectively, the intercept and slope of a \( Y \) vs \( n \) plot. Here
\[
Y = \ln(M_0 - M_{eq})
\tag{8a}
\]
\[
e^{e} = \frac{M_0 - M_{eq}}{M_0 - M_{\infty}}
\tag{8b}
\]
\[
e^S = e^{-T_1 \gamma} \left[ 1 + \frac{(M_{eq} - M_{\infty})/M_{eq}}{M_{eq} - M_{eq}} \right] - \left[ \frac{(M_{eq} - M_{\infty})/M_{eq}}{M_{eq} - M_{eq}} \right].
\tag{8c}
\]

It should be remarked here that Eqs. (8) hold only for the case \( 0 \leq X \leq 1 \) since otherwise the expression in square brackets in Eq. (6) would be negative and logarithms would not be permissible. For \( 1 \leq X \leq 2 \), i.e., the case for which the magnetization is partially or fully reversed by a passage (or pulse), it may be easily shown that a plot of \( \ln(M_0 - M_{eq}) \) vs \( n \) has an intercept given by \( e^S = \left| \frac{M_0 - M_{eq}}{M_0 - M_{\infty}} \right| \), and a slope \( S' \) given by \( e^{S'} = \left[ \text{right hand side of Eq. (8c)} \right] \).

If \( M_0 = M_{eq} \), then Eqs. (8b) and (8c) may be quickly solved for \( T_1 \); this was the case assumed in Ref. 1. However, if \( M_0 > M_{eq} \), due to initiation of the train of passages before equilibrium is reached, still the slope of the \( \ln(M_0 - M_{eq}) \) vs \( n \) plot is the same since it does not depend upon \( M_0 \). Unfortunately, there are now two unknowns, \( M_{eq} \) and \( T_1 \), but we can easily relate \( M_{eq} \) to \( M_0 \). Before doing this we note a special case, \( X = 2 \) (adiabatic reversal and \( \tau/T_1 \ll 1 \)). Then by Eq. (5), \( M_{eq} \approx 0 \), and therefore by Eq. (6), \( M_0 \approx M_0 e^{-e^{T_1 \gamma} / T_1} \). This result was derived by Santini and applied in the study of \( T_1 \) in liquid \(^3\)He.

For the general case we define \( T \) as the off-resonance “waiting” time and \( M \) as the magnetization at the beginning of the waiting time. Then
\[
M_0 = M_{eq} (1 - e^{-T_1 \gamma}) + M e^{-T_1 \gamma}.
\tag{9}
\]

This relates \( M_0 \) to \( M_{eq} \) and Eq. (8c) can then be solved for \( T_1 \). However, in the usual experimental situation \( M \) will be the last signal in the preceding train. If the train is long enough, then \( M = M_{eq} + M_{eq} (1 - X) \). Since, according to Eq. (6), \( e^S = (1 - X) e^{-T_1 \gamma} \), we use Eq. (5) to get
\[
M_{eq} (1 - X) = M_{eq} [(1 - e^{-T_1 \gamma}) / (1 - e^S)] e^{S e^{T_1 \gamma}} \]
\[
(1 - e^{-T_1 \gamma}) / (1 - e^S) \right] e^{S e^{T_1 \gamma}} \]
\[
and thus, by Eq. (9),
\[
M_{eq} = M_0 \left[ 1 - \left( 1 - e^{-T_1 \gamma} \right) / (1 - e^S) \right]^{-1}.
\tag{11}
\]

Then, from Eqs. (8c) and (11),
\[
e^{-T_1 \gamma} = 1 - \left( 1 - e^S \right) \left( M_{eq} / M_0 \right) \left[ 1 - C(\gamma) \right],
\tag{12}
\]

which can be solved for \( T_1 \) using the experimental parameters, \( \tau \) and \( T \), those given by the data, \( M_{eq} \) and \( M_0 \), and the calculated slope \( S' \) of an \( \ln(M_0 - M_{eq}) \) vs \( n \) plot.

II. Iteration

It is generally more convenient to solve Eq. (12) iteratively if \( T \geq T_1 \) since the second term in square brackets is clearly a corrective term which is small when \( T \) is large, making \( M_0 \) close to \( M_{eq} \). Thus, defining the successive approximations to \( T_1 \) as \( T_1^{(1)}, T_1^{(2)}, T_1^{(3)}, \ldots \), we cyclically solve
\[
e^{-T_1^{(n+1)}} = 1 - \left( 1 - e^S \right) \left( M_{eq} / M_0 \right) \left[ 1 - C^{(n)} \right],
\tag{13a}
\]
\[
C^{(n)} = \left( 1 - e^S \right) e^{-T_1^{(n)}} / (1 - e^S),
\tag{13b}
\]

letting \( C^{(0)} = 0 \). The first few terms are
\[
e^{-T_1^{(1)}} = 1 - \left( 1 - e^S \right) M_{eq} / M_0
\tag{14a}
\]
\[
C^{(1)} = \left( 1 - e^S \right) e^{-T_1^{(1)}} / (1 - e^S),
\tag{14b}
\]
\[
e^{-T_1^{(2)}} = 1 - \left( 1 - e^S \right) M_{eq} / M_0 (1 - C^{(1)}).
\tag{14c}
\]

The convergence is generally quite rapid. In one example (\(^{19}\)F in CaF\(_2\)) which the authors chose at random, the parameters were \( T_1 = 0.125 \) sec (true \( T_1 \)), \( e^S = 0.688 \), \( \tau = 0.025 \) sec, \( M_{eq} / M_0 = 0.675 \), and \( T = 0.164 \pm 0.357 \) sec. Then, using Eqs. (13a) and (13b), we got \( T_1^{(1)} = 0.106 \) sec, \( T_1^{(2)} = 0.122 \) sec, \( T_1^{(3)} = 0.124 \) sec, and \( T_1^{(4)} = 0.125 \) sec. Thus, with only three iterations the \( T_1 \) value was within 1% of the correct value and the data accumulation time was only about one half of that required to insure \( M_0 = M_{eq} \). In another example (\(^{19}\)F in CaF\(_2\)) which the authors chose at random, the parameters were \( T_1 = 2.50 \) sec, \( e^S = 0.580 \), \( \tau = 0.0625 \) sec, \( M_{eq} / M_0 = 0.0974 \), and \( T = 2.23 \pm 0.8971 \) sec. The iterations gave \( T_1^{(1)} = 1.49 \) sec; \( T_1^{(2)} = 1.48 \) sec; \( T_1^{(3)} = 2.48 \) sec; thus, after seven iterations the \( T_1 \) value was less than 1% low and the data accumulation time was only about one fourth that normally required.

Although in the above examples the \( T_1 \) measurement time would not be long by any method, it is apparent that if it is expected to be long, due to a large \( T_1 \), the method described in this paper has significant advantages since it is not necessary to wait for spin system equilibrium before taking data. The iterations are easily programmed on a computer.\(^6\)

\(^6\) Interested persons may obtain the computer program (FORTRAN IV, XTRAN, or CAL) from the authors.