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 τ 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 nth passage (or pulse). Furthermore, define the fraction of saturation, X, due to a passage (or pulse) by

$$M_n^+ = M_n^-(1-X), \quad 0 \le X \le 2, \tag{1}$$

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

$$\begin{aligned} M_{n+1}^- &= M_{eq}^-(1-e^{-\tau/T_1}) + M_n^+ e^{-\tau/T_1} \\ &= M_{eq}^-(1-e^{-\tau/T_1}) + M_n^-(1-X)e^{-\tau/T_1}, \end{aligned} \tag{2}$$

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

$$\begin{aligned} M_1^- &= M_{eq}^-(1-u) + M_0^- yu \\ M_2^- &= M_{eq}^-(1-u)[1+yu] + M_0^- y^2u^2 \\ &\vdots \\ M_n^- &= M_{eq}^-(1-u)[1+yu+y^2u^2 \cdots y^{n-1}u^{n-1}] \\ &\quad + M_0^- y^n u^n. \end{aligned} \tag{3}$$

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

$$\begin{aligned} M_n &= M_{eq}(1-u)\sum_{q=0}^{n-1} y^q u^q + M_0 y^n u^n \\ &= M_{eq}(1-u)\frac{1-y^n u^n}{1-yu} + M_0 y^n u^n. \end{aligned} \tag{4}$$

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

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

and, thus,

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

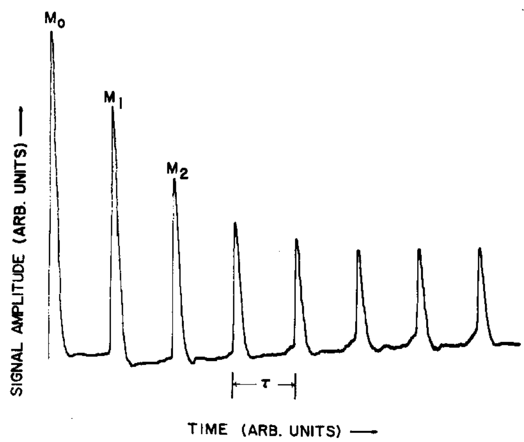

FIG. 1. A recorder tracing of a train of free induction decays in Mn^{2+}-doped H_2O, each decay following a pulse of about 48°. The time between pulses is τ. For details of the calculation of T_1 see the text and Ref. 4.

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or, using Eq. (5) to solve for $X\equiv 1-y$,

$$(M_n-M_\infty)=(M_0-M_\infty)\left[e^{-\tau/T_1}\left(1+\frac{M_{eq}-M_\infty}{M_\infty}\right)-\left(\frac{M_{eq}-M_\infty}{M_\infty}\right)\right]^n. \quad (7)$$

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

$$Y=\ln(M_n-M_\infty) \quad (8a)$$

$$e^I=(M_0-M_\infty) \quad (8b)$$

$$e^S=e^{-\tau/T_1}[1+(M_{eq}-M_\infty)/M_\infty]-[(M_{eq}-M_\infty)/M_\infty]. \quad (8c)$$

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 $\ln|M_n-M_\infty|$ vs n has an intercept given by $e^I=|M_0-M_\infty|$, and a slope S' given by $e^{S'}=-$[right hand side of Eq. (8c)].

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 $\ln(M_n-M_\infty)$ 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), $M_\infty\simeq 0$, and therefore by Eq. (6), $|M_n|\simeq M_0e^{-n\tau/T_1}$. This result was derived by Santini[5] and applied in the study of T_1 in liquid ^3He.

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

$$M_0=M_{eq}(1-e^{-T/T_1})+Me^{-T/T_1}. \quad (9)$$

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 $M=M_\infty^+=M_\infty^-(1-X)$. Since, according to Eq. (6), $e^S=(1-X)e^{-\tau/T_1}$, we use Eq. (5) to get

$$M_\infty(1-X)=M_{eq}[(1-e^{-\tau/T_1})/(1-e^S)]e^Se^{\tau/T_1}, \quad (10)$$

and thus, by Eq. (9),

$$M_{eq}=M_0\{1-[(1-e^Se^{\tau/T_1})e^{-T/T_1}/(1-e^S)]\}^{-1}. \quad (11)$$

[5] M. Santini, Nuovo Cimento 16, 232 (1960).

Then, from Eqs. (8c) and (11),

$$e^{-\tau/T_1}=1-(1-e^S)\frac{M_\infty}{M_0}\left[1-\frac{(1-e^Se^{\tau/T_1})e^{-T/T_1}}{1-e^S}\right], \quad (12)$$

which can be solved for T_1 using the experimental parameters, τ and T, those given by the data, M_∞ and M_0, and the calculated slope S of an $\ln(M_n-M_\infty)$ vs n plot.

II. ITERATION

It is generally more convenient to solve Eq. (12) iteratively if $T\gtrsim T_1$ 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 $T_1^{(1)}$, $T_1^{(2)}$, $T_1^{(3)}\cdots$, we cyclically solve

$$e^{-\tau/T_1^{(n+1)}}=1-(1-e^S)(M_\infty/M_0)[1-C^{(n)}], \quad n\geq 0 \quad (13a)$$

$$C^{(n)}=(1-e^Se^{\tau/T_1^{(n)}})e^{-T/T_1^{(n)}}/(1-e^S), \quad n\geq 1 \quad (13b)$$

letting $C^{(0)}\equiv 0$. The first few terms are

$$e^{-\tau/T_1^{(1)}}=1-(1-e^S)M_\infty/M_0 \quad (14a)$$

$$C^{(1)}=(1-e^Se^{\tau/T_1^{(1)}})e^{-T/T_1^{(1)}}/(1-e^S) \quad (14b)$$

$$e^{-\tau/T_1^{(2)}}=1-(1-e^S)(M_\infty/M_0)(1-C^{(1)}). \quad (14c)$$

$$\vdots$$

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, $M_\infty/M_0=0.675$, and $T=0.164\simeq 1.35T_1$. Then, using Eqs. (13a) and (13b), we got $T_1^{(1)}=0.106$ sec, $T_1^{(1)}=0.122$ 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 (^1H in H_2O) the parameters were $T_1=2.50$ sec, $e^S=0.580$, $\tau=0.0625$ sec, $M_\infty/M_0=0.0974$, and $T=2.23$ sec$\simeq 0.89T_1$. The iterations gave $T_1^{(1)}=1.49$ sec$\cdots$, $T_1^{(7)}\simeq 2.48$ 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.