NON-STATIONARY PHENOMENA IN NUCLEAR MAGNETIC RESONANCE

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The "ringing" of a nuclear spin system produced by a unit pulse, and by a triangular pulse is considered and calculations are made of transient processes caused by jumps in frequency which simulate the phenomenon of the "beating of beats". It is shown that a transient process in a spin system is determined only by the properties of the latter and not by the shape of the radio frequency pulse. Formulas are obtained which may be used to measure relaxation times.

THE application of nuclear magnetic resonance methods to the study of the nature of the liquid state has made it possible to obtain additional information about processes occurring in liquids.

In spite of the fact that recently Bloch[1] succeeded in giving a quantum theory of transient phenomena in nuclear magnetic resonance the most useful description of these phenomena is still the one given within the framework of classical theory also by Bloch[2] who derived on the basis of Ehrenfest's theorem his well known equations describing the behavior of the nuclear magnetization vector in external fields.

Bloch's equations hold sufficiently accurately in the case of liquids[3,4] even though in deriving them no account is taken of the fact that the magnetization of a substance is associated with a decrease in the entropy of the spin system. Taking into account the principle of minimum entropy leads to the appearance in Bloch's equations of only a small additional term.[5]

The solution of Bloch's equations has been investigated by different methods in a number of special cases.[2,6,7] However, these cases do not cover all aspects of the phenomenon since the nuclear induction method has now found a new application. One should first of all refer to the observation of the effect of free nuclear induction in the earth's magnetic field,[8] and also to the use of pulse methods for the measurement of relaxation times. The general solution of the nuclear induction problem has not been given in the literature for the above cases. It is also of considerable interest to investigate the behavior of a spin system when pulsed signals of various shapes are applied to the sample.

In this connection in the present paper we obtain by the methods of operational calculus[9] solutions of Bloch's equations which may be employed for the measurement of relaxation times and also for the simulation of transient processes in a nuclear spin system by processes taking place in certain four terminal networks.

1. FORMULATION OF THE PROBLEM

The system of Bloch's equations is a system of linear differential equations with variable coefficients. In order to observe nuclear resonance signals by the steady state method, a sinusoidal modulation of the magnetic field is used. If the modulation amplitude is small then the variable part of the magnetic field $H(t)$ is small in comparison with the constant component H_0:

$$H(t) = H_0 + H_m \sin \omega_m t, \tag{1}$$

where ω_m is the modulation frequency.

When the weak radiofrequency field which gives rise to the precession of the macroscopic nuclear magnetization vector M is directed at right angles to the strong magnetic field, Bloch's system of equations may be put in the form

$$\begin{gathered} du/dt + \Delta\omega v + u/T_2 = 0, \\ dv/dt - \Delta\omega u + \gamma H_1 M_z + v/T_2 = 0, \\ dM_z/dt - \gamma H_1 v + M_z/T_1 = M_0/T_1, \\ H_x = H_1 \cos \omega t, \ H_y = \mp H_1 \sin \omega t, \end{gathered} \tag{2}$$

where u is the dispersion mode signal, v is the absorption mode signal, T_2 is the transverse relaxation time, T_1 is the longitudinal relaxation time, M_0 is the static value of nuclear polarization, $\Delta\omega$ is the detuning and γ is the gyromagnetic ratio. If sinusoidal modulation of the magnetic field is employed, the detuning will have the form

$$\Delta\omega(t) = \gamma H_m \sin \omega_m t. \tag{3}$$

Since the amplitude of the modulation of the magnetic field is small, it may be assumed to a sufficient degree of accuracy that $M_0 = \text{const}$. In the cases of linear detuning $\gamma H_m \omega_m t$, and sinusoidal detuning $\gamma H_m \sin \omega_m t$, the operational method yields respectively integrals of the form

$$\gamma H_m \omega_m \int_0^\infty t v(t) e^{-pt}\, dt = -\gamma H_m \omega_m \frac{dv(p)}{dp},$$

$$\gamma H_m \int_0^\infty \sin \omega_m t v(t) e^{-pt}\, dt$$

$$= \frac{\gamma H_m}{2i} \frac{v(p - i\omega_m)(p + i\omega_m) - v(p + i\omega_m)(p - i\omega_m)}{p^2 + \omega_m^2}. \quad (4)$$

Below we discuss the solution of Bloch's equations for certain special cases of practical importance.

2. THE CASE OF ADIABATIC PASSAGE THROUGH THE RESONANCE REGION

We consider the case when $\Delta\omega$ is a slowly varying function, while the relaxation times T_1 and T_2 are sufficiently large that the criterion for rapid passage in Bloch's sense remains satisfied. The condition on the slowness of variation of $\Delta\omega$ is

$$d\Delta\omega / dt \ll \gamma^2 H_1^2. \quad (5)$$

This condition is satisfied more and more accurately as the level of the radio frequency field is raised. The slowness of variation of $\Delta\omega$ does not determine the conditions for the slowness of passage through the resonance region since these conditions also presuppose short relaxation times.[2]

It is well known that the Laplace transformation is applicable to all functions bounded in the interval from zero to infinity or increasing as t^a, or even as e^{at}, where a is some positive number. Any arbitrary physical function satisfies these conditions, and therefore by multiplying Bloch's equations from the left and from the right by e^{-pt} and integrating from zero to infinity we obtain the transformed equations

$$\begin{aligned} &(p + 1/T_2) u(p) + \Delta\omega v(p) = u(0), \\ &(p + 1/T_2) v(p) - \Delta\omega u(p) + \gamma H_1 M_z(p) = v(0), \\ &(p + 1/T_1) M_z(p) - \gamma H_1 v(p) = M_0 / T_1 p + M_z(0), \end{aligned} \quad (6)$$

where $u(0)$ is the initial value of the dispersion mode signal, $v(0)$ is the initial value of the absorption mode signal and $M_z(0)$ is the initial value of nuclear polarization along the z axis.

In order to solve this system of equations, we must evaluate its determinant

$$\begin{aligned} \Delta(p) &= (p + 1/T_2)^2 (p + 1/T_1) \\ &+ (\Delta\omega)^2 (p + 1/T_1) + (\gamma H_1)^2 (p + 1/T_2). \end{aligned} \quad (7)$$

We limit ourselves to a discussion of the absorption mode signal $v(p)$ and use the inverse Laplace transformation for the determination of $v(t)$. The Riemann-Mellin integral is evaluated by means of residues, and for this we have to find the roots of the characteristic equation

$$\Delta(p) = 0. \quad (8)$$

This is a cubic equation with real coefficients and therefore it has at least one real root; it may be easily shown that the other two roots are imaginary in the present case.

We denote the real root of (8) by α and write the determinant of the system in the form

$$\Delta(p) = (p + \alpha)[(p + \beta)^2 + \eta^2], \quad (9)$$

where β and η are certain arbitrary constants. By decomposing the rational fraction $v(p) = \Delta_2(p)/\Delta(p)$ into the simplest fractions and utilizing the inverse Laplace transformation, we shall obtain the expression for the absorption mode signal:

$$v(t) = Ae^{-\alpha t} + Be^{-\beta t} \cos \eta t + (C/\eta) e^{-\beta t} \sin \eta t + D, \quad (10)$$

where A, B, C, D are arbitrary constants. The dispersion mode signal will also have a similar form. The arbitrary constant D may be evaluated from the condition

$$D = v(p)\, p \quad \text{as} \quad p \to 0. \quad (11)$$

D represents the stationary solution of Bloch's equations and its form coincides with the solution obtained by Bloch by a different method.[2]

From a comparison of the coefficients one may easily obtain relations also for the other arbitrary constants:

$$\begin{aligned} &A + B + D = v(0); \\ &2A\beta + B\beta + C + B\alpha + 2\beta D + D\alpha \\ &= v(0)(1/T_1 + 1/T_2) - \gamma H_1 M_z(0) + u(0)\Delta\omega, \\ &A\beta^2 + A\eta^2 + B\alpha\beta + C\alpha + D\eta^2 + 2\beta\alpha D + D\beta^2 \\ &= v(0)/T_2 T_1 + u(0)\Delta\omega / T_1 - \gamma H_1 M_0 / T_1 - \gamma H_1 M_z(0)/T_2; \\ &2\beta + \alpha = 2/T_2 + 1/T_1; \\ &\eta^2 + \beta^2 + 2\beta\alpha = 1/T_2^2 + 2/T_1 T_2 + (\Delta\omega)^2 + (\gamma H_1)^2; \\ &\alpha(\eta^2 + \beta^2) = 1/T_2^2 T_1 + (\Delta\omega)^2 / T_1 + (\gamma H_1)^2 / T_2. \end{aligned} \quad (12)$$

Thus the solution of Bloch's equations consists of terms describing the transient process as well as a stationary term.

Calculations on a molecular basis lead to the conclusion that the relaxation times T_1 and T_2 must be of the same order of magnitude. In practice, because of the inhomogeneity of the magnetic field, considerable deviations from this rule can occur. Since there was no perpendicular polarization before resonance, $u(0) = v(0) = 0$. Then in the case that $T_2 \sim T_1$ we have:

$$v(t) = [\gamma H_1 M_0 / ((\Delta\omega)^2 T_2 + 1/T_2$$

$$+ (\gamma H_1)^2 T_1)]e^{-t/T_2}\cos\sqrt{(\gamma H_1)^2 + (\Delta\omega)^2}\, t + [\gamma H_1 M_0/((\Delta\omega)^2 T_2 + 1/T_2 + (\gamma H_1)^2 T_1)]e^{-t/T_2}\sin\sqrt{(\gamma H_1)^2 + (\Delta\omega)^2}\, t - \frac{\gamma H_1 M_0}{(\Delta\omega)^2 T_2 + 1/T_2 + (\gamma H_1)^2 T_1}. \quad (13)$$

From this expression it may be seen that the exponential e^{-t/T_2} is the envelope of the transient processes while their frequency is determined by the detuning and increases as the detuning becomes greater.

Similarly in the case of very small detuning we obtain

$$v(t) = \left(v(0) + \frac{\gamma H_1 M_0}{1/T_2 + (\gamma H_1)^2 T_1}\right) \times \exp\left\{-\frac{1}{2}(1/T_2 + 1/T_1)t\right\}\cos\eta t + \left[\frac{v(0)}{2}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) + \frac{\gamma H_1 M_0}{1/T_2 + (\gamma H_1)^2 T_1}\left(\frac{1}{T_1} + \frac{2}{T_2}\right) - \gamma H_1 M_z(0)\right] \times \left[(\gamma H_1)^2 - \frac{1}{4}(1/T_2 - 1/T_1)^2\right]^{-1/2} \quad (14)$$
$$\times \exp\left\{-\frac{1}{2}\left(\frac{1}{T_2} + \frac{1}{T_1}\right)t\right\}\sin\eta t - \frac{\gamma H_1 M_0}{1/T_2 + (\gamma H_1)^2 T_1}.$$

Observation of transient processes enables one to determine the relaxation times. However, in the steady state method their realization in a pure form is associated with considerable experimental difficulties.

3. PULSE METHODS IN NUCLEAR MAGNETIC RESONANCE

Transient phenomena in nuclear magnetic resonance may be realized by means of applying the radio frequency field in the form of pulses. For the case when the signal is observed during pulses of radio frequency field lying within the resonance band ($\Delta\omega = 0$), one can use expression (14). In this case the solution is obtained without any simplifying assumptions since the system of Bloch's equations reduces to a system of equations with constant coefficients. When the radio frequency field is large and the stationary term becomes saturated the nuclear resonance signal during the pulses will have the form

$$v(t) = \frac{-\gamma H_1 M_z(0)}{\sqrt{(\gamma H_1)^2 - {}^1/_4(1/T_2 - 1/T_1)^2}}\exp\left\{-\frac{1}{2}\left(\frac{1}{T_1} + \frac{1}{T_2}\right)t\right\} \times \sin\sqrt{(\gamma H_1)^2 - {}^1/_4(1/T_2 - 1/T_1)^2}\, t. \quad (15)$$
$$v(0) = u(0) = 0.$$

From the above expression it may be seen that the envelope of the signal is given by the exponential e^{-t/T_0} with $1/T_0 = \frac{1}{2}(1/T_1 + 1/T_2)$, while the oscillation frequency is always given by the nuclear Larmor precession frequency. Since the signal is observed after appropriate detection, the above fact enables one to determine the overall relaxation time T_0.

In the case when the frequency of the r.f. field is not exactly equal to the nuclear Larmor precession frequency expression (13) may be used to describe the absorption mode signal.

Expressions (13), (14) and (15) represent the response of a spin system to an r.f. pulse which may be considered to be a unit pulse. The absorption mode signal will then represent the envelope of the process whose frequency is the nuclear Larmor precession frequency.

Thus the use of the phenomenological Bloch equations as the starting point enables us to calculate the response of a spin system to a unit r.f. pulse, and consequently also to a signal of arbitrary form, since the spin system possesses resonance properties.

In order to investigate the question of the effect of a pulse of triangular shape, we shall use the formula

$$D(t) = E(0)\, v(t) + \int_0^t v(\tau) E'(t-\tau)\, d\tau, \quad (16)$$

where $D(t)$ is the envelope of the output signal, $E(t)$ is the envelope of the input signal and $v(t)$ is the response of the system to a unit r.f. pulse. In the present case, it is sufficient to investigate a linearly increasing input voltage $E = at$. We then obtain

$$D(t) = a\int^t v(\tau)\, d\tau = A'[e^{-bt}(-b\sin\eta t - \eta\cos\eta t) + \eta]/(b^2 + \eta^2). \quad (17)$$

It may be seen from this expression that the envelope of the transient processes remains of the form e^{-t/T_0} also in the case of a triangular pulse, i.e., the "damping" of the transient process is independent of the shape of the r.f. pulse and is determined only by the properties of the spin system.

If the nuclear magnetic resonance signal is observed in the interval between pulses of the r.f. field then the following conditions hold

$$\Delta\omega = \gamma H_0, \; H_1 = 0. \quad (18)$$

In this case we can obtain for the absorption mode signal

$$v(t) = e^{-t/T_2}(v(0)\cos\gamma H_0 t + u(0)\sin\gamma H_0 t). \quad (19)$$

Similarly, the dispersion mode signal is described by the expression

$$u(t) = e^{-t/T_2}(u(0)\cos\gamma H_0 t - v(0)\sin\gamma H_0 t). \quad (20)$$

Thus observation of nuclear resonance signals both during the pulses and in the interval between the pulses of the r.f. field enables us to determine both the longitudinal and the transverse relaxation times.

The expressions obtained for the dispersion and absorption mode signals in the interval between pulses may be used for the description of signals of free nuclear induction observed in weak magnetic fields. In order to obtain transverse polarization in this method a sufficiently strong magnetic field perpendicular to the weak one is used. For the perpendicular component of nuclear polarization we obtain

$$M_y = \mp e^{-t/T_2}[v(0)\cos\gamma H_0 t + u(0)\sin\gamma H_0 t]. \quad (21)$$

Then the following nuclear induction signal will appear across the terminals of the receiver coil

$$v(t) = \mp \frac{4\pi}{c} NS\gamma H_0 v(0)\, e^{-t/T_2}\cos\gamma H_0 t, \quad (22)$$

where N is the number of turns in the receiver coil and S is its cross-section area.

Consequently the observation of free nuclear induction signals in the earth's field permits one to determine the transverse relaxation time very accurately since the earth's field has a high degree of natural homogeneity.

In order to carry out calculations for transient processes in a spin system in the case of sudden jumps of frequency we shall assume that initially an r.f. field characterized by the detuning $-\Delta\omega$ was switched on, that it was switched off at the time $T = 0$, and another r.f. field detuned by an amount $+\Delta\omega$ was switched on. Then for large T we can obtain

$$D(t)\, e^{i\omega_0 t} = v(t+T, -\Delta\omega)\, e^{i(\omega_0-\Delta\omega)t} - v(t, -\Delta\omega)\, e^{i(\omega_0-\Delta\omega)t} + v(t, +\Delta\omega)\, e^{i(\omega_0+\Delta\omega)t}. \quad (23)$$

From this we obtain for the nuclear resonance signal

$$D(t) = -[\gamma H_1 M_0 / ((\Delta\omega)^2 T_2 + 1/T_2 + (\gamma H_1)^2 T_1)] \times [1 - 2ie^{-t/T_2}(\cos\eta t + (1/T_2\eta)\sin\eta t)\sin\Delta\omega t]. \quad (24)$$

It may be seen from this that transient processes in the case of frequency jumps are of a more complicated nature, i.e. additional oscillations of the envelope of the nuclear magnetic resonance signals are now observed. Transient processes associated with jumps of frequency remind one by their shape of the phenomenon of "beating of beats" due to the presence in the sample of groups of resonating nuclei with different precession frequencies. This fact makes it much more difficult to observe the "beating of beats". It should be noted that in stationary nuclear resonance methods associated with a deviation of frequency the transient phenomena are always somewhat distorted. Small drifts of the generator frequency sometimes make it possible to observe the pseudo-phenomenon of "beating of beats" even in pure water.

The cases considered above show that transient phenomena in a spin system are similar to transient processes in coupled resonant electrical circuits. The expressions obtained above are simple and may be used for the experimental determination of relaxation times.

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