Corrections to the Expression of a Sample Magnetization Under A Radiofrequency Magnetic Field[1]

Ariel Kaplan, Eduardo Gonzalez and Gustavo S. Garcia Andrada[2]
Facultad de Matemática, Astronomia y Fisica (IMAF).
Universidad Nacional de Córdoba.
Laprida B54. 5000 Cordoba, Argentina

Contents

I. Introduction

The magnetization of a sample under a radiofrequency magnetic field is studied for a two level system. The Bloch and Siegert's differential equations (1) are developed and the double frequency terms are taken into account. The proposed solutions are a series expansion in Ω_o/Ω_1 and the corrections to be introduced in the expression for the magnetization are calculated. The possibility of an experimental verification of these facts is proposed.

1. In NMR as well as in NQR (2,3), the Hamiltonian can be written as $H = H_o + H_p(t)$. In both cases, $H_p(t)$ will be oscillating rf field that, for simplicity's sake, will be taken along the X axis.

Then

$$H_p(t) = -\gamma\ H_1\ \cos \omega t\ J_x$$

By taking the particular cases: NMR, with I = 1/2, and NQR, with I=1, the system will be a two level one, for both cases. Then, it will follow the same equations with just a parameter adjustment.

By calling those two levels by α and β, the development coefficients of the wave function will satisfy, in resonance, the following equations:

$$\dot{c}_\alpha(t) = \mathrm{ib}\ [1 + \exp(-\mathrm{iat})]\ c_\beta(t),$$

$$\dot{c}_\beta(t) = \mathrm{ib}\ [1 + \exp(\mathrm{iat})]\ c_\alpha(t),$$

where $b \propto \gamma H_1 = \Omega_1$ and $a \propto \Omega_o$ (resonant frequency).

[1]Partially supported by Consejo Nacional de Investigaciones Cientificas y Tecnicas, Argentina.

[2]Comision Nacional de Energia Atomica, Buenos Aires, Argentina.

As a rule, when solving those equation systems, the terms containing the factor $\exp(\pm 2i\Omega_o)$ are neglected (2,3). These terms are called the double frequency terms.

The experimental conditions are such that $\Omega_1 << \Omega_o$ and $\Omega_o t_w >> 2\pi$, where t_w is the rf pulse width. The effect of the double frequency terms is to produce oscillations of a frequency $2\Omega_o$, superposed to an oscillating solution of frequency Ω_1, and of little relative amplitude. Then, this effect in a great number of oscillations (of a double frequency) is averaged to zero, in a first approximation.

In this work, the influence of the double frequency terms is studied on the solutions of low frequency obtained by neglecting those terms. As a solution a series expansion in Ω_1/Ω_o is proposed, and the corrections to be introduced in the expression for the *magnetization* are calculated.

II. Resolution of the Equations

A. Form of the Solutions

It is convenient to write the equations in a matrix form. By defining

$$X(t) = \begin{bmatrix} c_\alpha(t) \\ c_\beta(t) \end{bmatrix}$$

it is obtained that $\dot{X}(t) = ibM(t)\,X(t)$, where

$$M(t) = \begin{bmatrix} 0 & 1+\exp(-\mathrm{i}at) \\ 1+\exp(\mathrm{i}at) & 0 \end{bmatrix} = M^+(t)$$

This is a first order linear differential equations system with time dependent coefficients. It is always possible to express the solution as

$$\chi(t) = Q(t)\chi_o.$$

By replacing in the wave equation, it follows that

$$\dot{Q}(t) = \partial Q/\partial t = \mathrm{ibM(t)Q(t)}$$

with the initial condition $Q(0) = 1$.

In general, $Q(t)$ will be a matrix that, taking into account the shape of $M(t)$, and the initial conditions for $Q(t)$, is

$$Q(t) = \begin{bmatrix} A(t) & -C^*(t) \\ C(t) & A^*(t) \end{bmatrix}$$

Hence, it is sufficient to know $A(t)$ and $C(t)$ in order to know $Q(t)$. At this point, it can be verified that the standard approximate solution (without considering the double frequency terms) is

$$A(t) = \cos bt$$

$$C(t) = i \sin bt$$

which will be equal to $c_\alpha(t)$ and $c_\beta(t)$, respectively, if the adequate boundary conditions are applied.

To consider the effect of the double frequency terms, it will be defined a parameter $\gamma = b/a$, to characterize the size of the perturbation term, compared to the principal hamiltonian term, which has typical values of the order of 10^{-2} to 10^{-3}.

After an interative study of these equations, we founded adequate to propose solutions of the form:

$$A(t) = \cos bt\ [1 + \gamma^2 F_2(at) + \gamma^4 F_4(at) + \ldots] +$$
$$i \sin bt\ [\gamma F_1(at) + \gamma^3 F_3(at) + \ldots]$$

$$C(t) = i \sin bt\ [1 + \gamma^2 G_2(at) + \gamma^4 G_4(at) + \ldots] +$$
$$\cos bt\ [\gamma G_1(at) + \gamma^3 G_3(at) + \ldots]$$

which reduces to the previous ones when $\gamma=0$. By introducing these solutions in the differential equations, calculating the corresponding derivatives and equating in the corresponding members, the terms containing sin bt and cos bt, respectively, the following equations are obtained:

$$\dot{F}_{n+1}(at) = i\ [1 + \exp(-iat)]\ G_n(at) - iF_n(at),$$

$$\dot{G}_{n+1}(at) = i\ [1 + \exp(iat)]\ F_n(at) - iG_n(at).$$

where the derivatives are taken with respect to the argument, at, and it is defined as

$$F_o(at) = G_o(at) \equiv 1.$$

B. Application of the Boundary Conditions to the Solutions

We have A(0) = 1, and C(0) = 0, and then

$$F_2(0) = F_4(0) = ... = F_{2n}(0) = 0,$$
$$G_1(0) = G_3(0) = ... = G_{2n+1}(0) = 0.$$

The rest of the initial conditions come from imposing physical requirements on the consecutive orders of γ in the solutions. The first requirement is to conserve the norm:

$$X^+(t)\ X(t) = 1,$$

i.e.:

$$|A(t)|^2 + |C(t)|^2 = 1.$$

The second requirement must be understood in the sense that if some terms, for $t \rightarrow \infty$ were divergent, they must be neglected,if possible, by means of an adequate choice of the constants. If this were not possible, it should be intended to minimize its influence, affecting them with a factor, as small as possible, consistent with the shape of the solutions.

By integrating the equations for the successives $\dot{F}$'s and $\dot{G}$'s, subjected to their respective initial conditions, and applying the already stated criteria to normalize the successive orders in γ, it is obtained:

$$F_1(at) = -\exp(-iat)$$
$$F_2(at) = \exp(iat) - 1$$
$$F_3(at) = -(1/2)\exp(-iat) - 2\exp(iat) - (1/2)\exp(-2iat) - (i/2)at$$
$$G_1(at) = \exp(iat) - 1$$
$$G_2(at) = -\exp(iat) + \exp(-iat) - 1/2$$
$$G_3(at) = \exp(-iat) + \exp(iat) + (1/2)\exp(2iat) - (1/2)\,at - 5/2$$

Then, it is impossible to eliminate completely the terms containing at on F_3 and G_3. This raises a problem, because it will introduce a divergent term on the third order expression for the magnetization when working with big values of t. But, if it is taken into account that $\gamma^3 at = \gamma^2 bt$, it can be thought that the divergent term will appear in the second order.

In the same way it is possible to write other divergent terms that will appear with higher order F's and G's. Thus, it is possible to say that the expressions already obtained for the F's and G's are not complete, but then the terms coming from the higher order expressions must be included. This difficulty is related with the criteria selected to impose the normalization.

Our interpretation is that these solutions are convergent in the asymptotic sense, whose validity is limited to a certain range of t. Particularly, in the solution to the second order, the condition $bt \simeq 1$ is getting a limit for its validity, because, for bigger values of t, it will be necessary to include a term coming from the third order, and so on. For the first order solution no validity conditions were found.

III. Calculus of the Magnetization

A. Magnetization after the First rf Pulse

Let us consider those solutions applied to a nuclear spin system, under a sequence of two rf pulses (for example: one of $\pi/2$ and the other of π). With them, the expression for the magnetization will be calculated, and the corrected free induction signals after the first and second pulses, as well as the echo signal will be obtained. In the case of the example it will be, for NQR, bt = $\pi/4$ and bt=$\pi/2$, respectively, and then, the validity condition for the second order solution will be very limited, principally for the free induction signal of the second pulse and of the echo. Then, the calculus will consider the second order expressions only for the free induction signal after the first pulse, and, in general, the calculus will be limited only to the solution in a first order.

To obtain the state of the system it is necessary to define $\tilde{\chi}t = F(t)\chi(t)$, where F(t) is a phase matrix:

$$F(t) = \begin{bmatrix} \exp(-i\omega_\alpha t) & 0 \\ 0 & \exp(-\omega_\beta t) \end{bmatrix}$$

with $\omega_\alpha = E_\alpha/\hbar, \omega_\beta = E_\beta/\hbar$, and $\omega_\alpha - \omega_\beta = \Omega_o$.

Supposing that, beginning from the initial state we apply an rf pulse, of a t_w width, the state of the system, for $t > t_w$, will be given by

$$\tilde{\chi}(t) = F(t)\ Q(t)\ \chi_o$$

and the density matrix will be

$$\rho = \tilde{\chi}\tilde{\chi}^{+} = \mathrm{F(t)\ Q(t)}\ \chi_o \chi_o^{+}\ \mathrm{Q(t_w)\ F^{+}(t)}.$$

For the expression of I_x, which is the really measured magnitude, the Pauli matrix will appear for NMR as well as for NQR, then the calculus will be completely analogous. The only difference will be an 1/2 factor, appearing in NMR, because of the I_x eigenvalue. Then

$$< I_x >= tr(\rho\sigma_x) = tr[\tilde{\chi}(t)\tilde{\chi}^{+}(t)\ \sigma_x],$$

By making the corresponding calculus it is possible to write, in a first approximation:

$$< I_x >= 2 \sin \Omega_o t\ |C^*(t_w)|$$

By making the calculus explicitly,

$$|A(t_w)\, C^*(t_w)| = \sin bt_w \cos bt_w\ R(t_w),$$

and then

$$< I_x >= \sin \Omega_o t \sin 2bt_w\ R(t_w),$$

where

$$R(t_w) = \{1 + 4\gamma \mathrm{sin} at_w\ \mathrm{ctg}2bt_w$$

$$+4\gamma^2[\mathrm{ctg}^2 2bt_w + \frac{1}{4}\mathrm{ctg}^2 bt_w - \mathrm{cos} at_w\ \mathrm{ctg}2bt_w\ \mathrm{ctg}bt_w$$

$$+\frac{1}{4}(2\mathrm{cos} at_w - 3)]\}^{1/2}.$$

In general, only the first order will be conserved in γ, and then only remain

$$R(t_w) = (1 + 4\gamma \sin at_w\ \mathrm{ctg}2bt_w)^{1/2} \qquad (1)$$

From this it follows immediately that the value of $< M_x >$ will be the classically obtained one, multiplied by the factor $R(t_w)$.

The inhomogeneities of the applied field and the random local field, in the NMR case, and stress and imperfections in the crystal, in the NQR case, will contribute to the fact that the different precession velocities produce dephasing and a consequent attenuation of the expectation value of the magnetization (Ref. 3 of the BHH[1]). It can be shown that, for typical experimental conditions, when carrying out the calculus explicitly, it is obtained:

$$M(t) \propto \sin 2bt_w \sin \Omega_o t \exp(-\delta^2 t^2/2)\ R(t_w) \qquad (2)$$

where δ is the standard deviation of the frequency distribution, i.e., in this approximation, after averaging over the sample, the same factor $R(t_w)$ appears.

B. Magnetization after the second rf Pulse and Echo

If, at t=T, a second rf pulse, of width t'_w is applied, the vector of state, for $t>T+t'_w$, will be

$$\tilde{\chi}(t) = F(t-T)\ Q(t'_w)\ F(t)\ Q(t_w)\ \chi_o.$$

We have that

$$< I_x >= tr(\tilde{\chi}\tilde{\chi}^{+}\ I_x).$$

Then, when the calculus is explicitly done there appears four terms for the magnetization. Two of them have a factor of the shape $\exp[i\Omega_o\ (t-T)]$ which, when making the calculus, gives

$$< I_x >= \sin[\Omega_o(t-T) \sin 2bt'_w\ \cos 2bt_w\ R(t_w, t'_w w).$$

where

$$R(t_w, t'_w) = (1 + 2\gamma\ [\mathrm{ctg}\ bt'_w \sin at'_w\ \mathrm{tg}\ bt'_w \sin at'_w -$$

$$-2\mathrm{tg}\ bt_w\ \mathrm{sin} at_w])^{1/2}.$$

From this formulae, when averaging over the sample, the free induction decay after the second pulse will be obtained.

Another of the terms has a factor of the shape $\exp[i\Omega_o(t-2T)]$, from where it is obtained

$$< I_x >= -\sin 2bt_w \sin bt'_w \sin[a(t-T)]\ R_{echo}, \qquad (3)$$

where

$$R_{echo} = (1 + 2\ [\mathrm{ctg}\ bt_w \sin at_w - \mathrm{tg}\ bt_w \sin at_w +$$

$$2\mathrm{ctg}\ bt'_w \sin at'_w])^{1/2}, \qquad (4)$$

from where, when averaged, a gaussian centered at t=2T will be obtained. This is the echo signal.

In both cases, when integrating over the sample volume, it is founded that the correction to the zeroth order is contained in the $R(t_w,t'_w)$ and R_{echo} factors, respectively. The same situation is found as for the free induction decay after the first pulse.

The fourth term has a factor of the shape a $\exp[i\Omega_o T]$ which, when averaged gives a gaussian centered at T=0. Then, for $t > T+t'_w$, this term will be negligible.

IV. Conclusions

It can be appreciated that there is a remarkable difference between the corrected formula and the zeroth order approximation - of sinusoidal shape - that results of not-considering the double frequency terms.

The influence of these double frequency terms increases with the parameter $\gamma=b/a$. By taking plausible values of γ, it is found that for $\gamma = .007$ the effect would be experimentally appreciable only with great difficulty, but for values of $\gamma=.04$ and of $\gamma=.07$ this effect would be experimentally verified.

For the free induction decay after the first pulse the calculus was done in a first and in a second order and no significant difference was found between both.

This suggests the possibility to realize the experimental verification of this effect, which would give place to an improvement of the experimental data interpretation.

V. Appendix I

A. Calculus for a Polycrystalline Sample

The equations we have worked are useful for single crystals, where the nuclear spin are oriented along a quantization axis, perpendicular to the rf coil axis. When working with polycrystalline samples, there is a distribution at random for the nuclear spins. Then, the quantization axis z will have, at their time, a random distribution in their orientations. Then, the nuclei will find their quantization axis z making an angle θ_1 with the rf coil. In that case, for a crystalline sample, the effective rf component will be $H_1 \sin\theta_1$ (2,4), where it must be integrated over all the possible values of θ_1.

B. Magnetization After the First rf Pulse and Echo after the Second rf Pulse

a) For the single crystal case it was obtained the magnetization after the first pulse as given by equations (1) and (2). For a powdered sample, integrating in a zeroth order [i.e.: neglecting $R(t_w)$], gives (1,2):

$$< M(t) > \propto \frac{8}{3} J_1(2bt_w) - \sum_{n=1}^{\infty}[J_{2n+1}(2bt_w)/(2n+1)(2n-1)(2n+3)]$$

where the $j_m(2bt_m)$ are Bessel Functions. This tells us that the maximum signal will be obtained with a 100 degrees pulse, instead of a $\pi/2$ pulse. In a first order, the integration must be carried out by taking into account the $R(t_w)$ factor.

b) For the echo, the result in the case of a single crystal is given by equations (3) and (4). Then, in a first order, the integration to be done is:

$$< M_x > \propto \int_0^{\pi} \sin^2\theta_1 \sin(2bt_w\sin\theta_1)\sin(bt'_w\sin(\theta_1)) \{(1+2\frac{b}{a}\sin\theta_1[ctg(bt_w\sin\theta_1)\sin at_w - tg(bt_w\sin\theta_1) \sin at_w + 2ctg(bt'_w\sin\theta_1)\sin at'_w])\}d\theta_1.$$

c) **Integration of the equations**

For the magnetization after the first pulse, the following integration must be done:

$$2\frac{b}{a}\sin at_w \int_0^{\pi} \sin^3\theta \cos(2bt_w\sin\theta)d\theta.$$

and the resultant final value for the magnetization after the first pulse will be given by

$$M(t) = \frac{8}{3}J_1(2bt_w) - \sum_{n=1}^{\infty}[J_{2n+1}(2bt_w)/(2n+1)(2n-1)(2n+3)] + 2\frac{b}{a}\sin at_w\{(\frac{4}{3}+\frac{3}{2}\sum_{k=1}^{\infty}(-i)^k (2bt_w)^{2k}.\{[1/(9).(-5).(25)...((2k)^2-9)] - [1/(3).(15).(35)...((2k)^2-1]\}.$$

Also here, it can be seen that the maximal obtainable signal is found for an rf pulse of the order of 100 degrees.

In this case, the evolution of the magnetization shows a behavior of the sinusoidal type.

C. Calculus of the echo signal

To solve this problem, it is necessary to integrate the four terms indicated in 3.2. Then, $< M_x >$, **in a first order** will be obtained:

$$< M_x > \propto \frac{\pi}{4}[J_o(2bt_w - bt'_w) - J_2(2bt_w - bt'_w)] - [J_o(2bt_w + bt'_w) - J_2(2bt_w + bt'_w)] + \frac{\pi}{2}\frac{b}{a}\{(\sin at_w + \sin at'_w)[3J_1(bt_w + bt'_w) - J_3(bt_w + bt'_w)] - (\sin at_w - \sin at'_w)[3J_1(bt_w - bt'_w) - J_3(bt_w - bt'_w)]\}.$$

The result of the first term, which is the factor of $\pi/4$, is the result of the calculus in zeroth order, and shows a sinusoidal shape, with a maximum for a pulse of the order of 100 degrees. The first order calculus shows, as it was in the single crystal case, a modulation over the sinusoidal shape of the magnetization.

Acknowledgments

To Dr. Lucien Guibé, for his critical observations of this work.

VI. References

[1]F. Bloch and A. Siegert, **Phys. Rev.** *57*, 522 (1940).

[2]M. Bloom, E.L. Hahnn and B. Hertzog, **Phys. Rev.** *97*, 1699 (1955).

[3]C.P. Slichter, **Principles of Magnetic Resonance**, Ch. II and Ch. IV, Springer-Verlag, 1978.

[4]D.E. Woessner and H.S. Gutowsky, **J. Chem. Phys.** *39*, 440 (1963).