

## Understanding NMR Pulse Sequences. Part 2. Variation of the Value of Liquid Magnetization with Spin

José Daniel Figueroa-Villar

Grupo de Química Medicinal, Departamento de Química, Instituto Militar de Engenharia, Praça General Tibúrcio 80, 22290-270, Rio de Janeiro, RJ, Brazil  
figueroa@ime.eb.br

**Keywords:** NMR theory, quadrupolar nuclei, spin magnetization

**Abstract:** The intensity of the NMR signals depends on the nuclear spin quantum number of the atom under investigation, but this correlation has not been shown in the literature. In this work, the first general equation for such correlation was deduced.

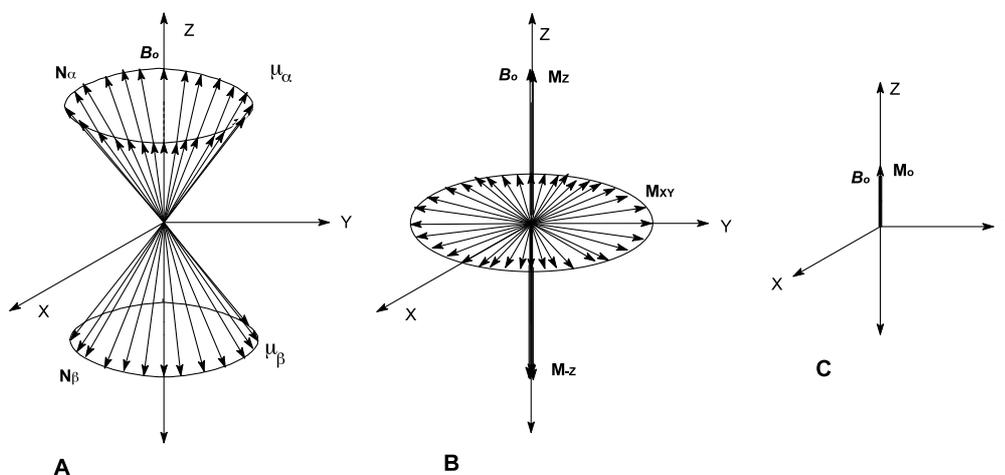
**Resumo:** A intensidade dos sinais de RMN depende do valor do número quântico de spin nuclear do átomo sob investigação, mas esta correlação não tem sido mostrada na literatura. Neste trabalho foi deduzida a primeira equação para esta correlação.

### Introduction

Liquid magnetization,  $M_o$ , is the representation of the maximum NMR signal that can be obtained using normal methods. We have already shown that the addition of all the magnetic moments of any sample inside a magnetic field leads to the liquid magnetization

$M_o$ , as shown in Figure 1 for a spin  $\frac{1}{2}$  sample.<sup>1,2</sup>

According to Figure 1, the value of  $M_o$  for spin  $\frac{1}{2}$  is given by Equation 1, where  $n_\alpha$  and  $n_\beta$  correspond to the populations of the system  $\alpha$  and  $\beta$  energy levels, respectively,  $\gamma$  is the magnetogiric constant and  $m_i$  is the magnetic nuclear spin quantum number.<sup>1,2</sup>



**Figure 1.** A) Distribution of the magnetic moments of a spin  $\frac{1}{2}$  sample. B) Addition of all the +Z, -Z and XY projections of all the magnetic moments. C) Addition of all the projections leading to the liquid magnetization  $M_o$ .

$$M_o = (n_\alpha - n_\beta) \gamma \hbar m_i \quad (1)$$

Because the value of  $m_i$  is  $+\frac{1}{2}$  for the  $\alpha$  magnetic moment and  $-\frac{1}{2}$  for the  $\beta$ , Equation 1 for spin  $\frac{1}{2}$  becomes

$$M_o = \frac{(n_\alpha - n_\beta) \gamma \hbar}{2} \quad (2)$$

In the previous paper<sup>2</sup> it was shown that the population difference between two energy

$$\frac{n_\beta}{n_\alpha} = 1 - \frac{\gamma \hbar B_o}{kT} \Rightarrow n_\alpha - n_\beta = n_\alpha \frac{\gamma \hbar B_o}{kT} \quad (4)$$

To use Equation 4 for the calculation of the  $n_\alpha - n_\beta$  value it is necessary to carry out an approximation: because  $n_\alpha + n_\beta = N$ , with  $N$  being the total number of spins in the sample and the energy difference  $\Delta E$  is a very low value, the population of both energy levels is almost the same, thus making possible to conclude that  $n_\alpha \cong n_\beta \cong N/2$ , and substitution of that value on Equation 1 leads to the complete expression of  $M_o$  for a spin  $\frac{1}{2}$  system (Equation 5):

$$M_o = \frac{N \gamma^2 \hbar^2}{4 kT} B_o \quad (5)$$

Equation 5 is extremely important, as it shows the direct dependence of  $M_o$ , and therefore of the signal intensity, from the number of atoms of interest in the sample ( $N$ ), the magnetogiric ratio ( $\gamma$ ) and the applied magnetic field strength

levels can be calculated from the Boltzman equation (Equation 3), where  $k$  corresponds to the Boltzmann constant ( $1.380\ 6504 \times 10^{-23}$  J.K<sup>-1</sup>).

$$\frac{n_\beta}{n_\alpha} = e^{-\frac{\Delta E}{kT}} \quad (3)$$

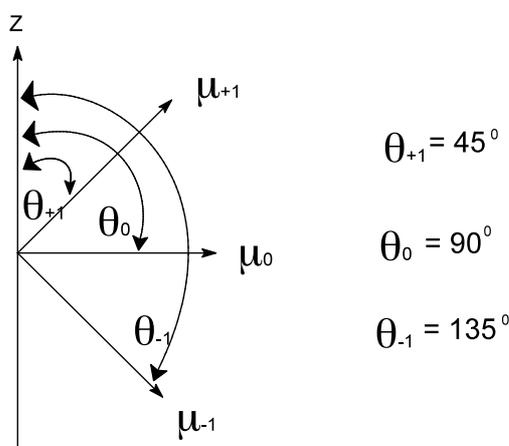
Considering that  $\Delta E/kT$  is almost zero, and that in NMR the  $\Delta E$  value is given by  $\gamma \hbar B_o m_i$  it is possible to convert Equation 3 to the non-exponential Equation 4:

( $B_o$ ). Accordingly, we have an explanation for the need of relatively concentrated samples for NMR analysis and the fact that NMR is a quantitative technique. It also explains the need for NMR spectrometers with higher magnetic fields and the fact that  $^1H$  is one of the most sensible nuclei in NMR. This equation also explains why the increase on the sample temperature ( $T$ ) decreases its signal intensity. However, the point of interest now is the fact that the value of  $M_o$  must change depending on the spin of the nuclei under examination. This is an important practical point in NMR because the use of NMR of nuclei with  $I > \frac{1}{2}$  is quite common. The important result for this topic would be the creation of an equation that could be used to predict the value of  $M_o$  for any system.

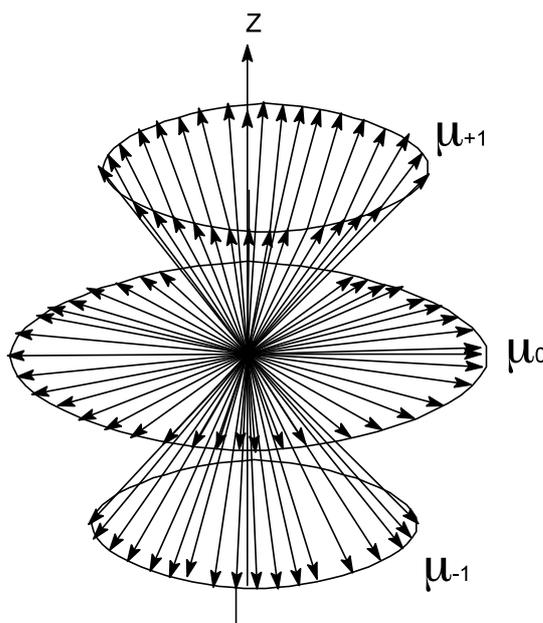
**Liquid magnetization for spin  $> \frac{1}{2}$**

Since the value of  $M_0$  must vary with the value of the spin quantum number, it is necessary to develop an equation for the prediction of this parameter. For nuclei with spin 1 the value of  $m_i$  can be **+1, 0** and **-1**, thus leading to three magnetic moment orientations, as shown in Figure 2. Accordingly, we have

three magnetic moment precession modes, which are shown in Figure 3. From this figure it can be easily concluded that the magnetic moments at the angle  $\theta_0$  do not contribute for the liquid magnetization value, therefore  $M_0$  must be calculated using the addition of the **Z**-projections of all the magnetic moments.



**Figure 2.** Allowed orientation for the magnetic moment ( $\mu$ ) for spin 1 nuclei.



**Figure 3.** Precession modes for spin 1 nuclei magnetic moments.

Because the projection of the magnetic moment at the Z direction is  $\mu_z = \lambda \hbar m_i$ , the three values for the magnetic moments of spin 1

nuclei are  $\mu_{+1} = \lambda \hbar$ ,  $\mu_{-1} = -\lambda \hbar$  and  $\mu_0 = 0$ , therefore, the liquid magnetization for this case is given by Equation 6:

$$M_o = n_{+1} \mu_{+1} + n_o \mu_o + n_{-1} \mu_{-1} = (n_{+1} - n_{-1}) \gamma \hbar \quad (6)$$

Also, the  $\Delta E$  value for the  $\mu_{+1}$  and  $\mu_{-1}$  corresponds to:

$$\Delta E = \gamma \hbar B_o \Delta m_i = 2 \gamma \hbar B_o,$$

and the population difference  $n_{+1} - n_{-1}$  is given by Equation 7.

$$n_{+1} - n_{-1} = \frac{2 N \gamma \hbar B_o}{3 kT} \quad (7)$$

Because there are three energy states for the spin 1 system, and considering that the population of all the levels is about the same, Equation 7 has the term  $N/3$ . Finally, the substitution of Equation 7 in Equation 6 gives

$$M_o = \frac{2 N \gamma^2 \hbar^2 B_o}{3 kT} \quad (8)$$

$$\begin{aligned} M_o &= n_{+3/2} \mu_{+3/2} + n_{+1/2} \mu_{+1/2} + n_{-1/2} \mu_{-1/2} + n_{-3/2} \mu_{-3/2} \\ M_o &= (n_{+3/2} - n_{-3/2}) \mu_{+3/2} + (n_{+1/2} - n_{-1/2}) \mu_{+1/2} \end{aligned} \quad (9)$$

$$n_{+3/2} - n_{-3/2} = \frac{N}{4} \frac{3 \gamma \hbar B_o}{kT} = \frac{3N}{2} \frac{\gamma \hbar B_o}{kT} \quad (10)$$

the value of  $M_o$  for the spin 1 system (Equation 8).

If the same calculation is carried out for spin 3/2 nuclei there are four energy levels, which are defined by the four values of  $m_i$ : +3/2, +1/2, -1/2 and -3/2. Because of this, the value for the approximated population for all the energy levels is  $N/4$ . The value for the liquid magnetization is given by Equation 9. The value of the population differences is also calculated using the Boltzman equation, as shown before for the spin 1/2 and 1 nuclei. Because the energy difference for the +3/2 and -3/2 levels is  $\frac{3 \gamma \hbar B_o}{kT}$ , the population difference between these energy levels is given by Equation 10.

For the +1/2 and -1/2 levels the population difference is given by Equation 11, which is different from the similar equation for the spin 1/2 nuclei because the number of energy levels is 4.

$$n_{+1/2} - n_{-1/2} = \frac{N \gamma \hbar B_o}{4 kT} \quad (11)$$

Knowing that the magnetic moments of Equation 9 are based on  $\mu_z = \gamma \hbar m_i$  their values are  $\mu_{+3/2} = \frac{3}{2} \gamma \hbar$  and  $\mu_{+1/2} = \frac{1}{2} \gamma \hbar$ , the whole value of  $M_o$  is expressed by Equation 12. In order to prepare a general equation for  $M_o$  it is still necessary to deduce the particular expression for other spin systems. The first one is the spin 2 nuclei. For this system, which

$$M_o = \frac{9N \gamma^2 \hbar^2 B_o}{8 kT} + \frac{N \gamma^2 \hbar^2 B_o}{8 kT} = \frac{10 N \gamma^2 \hbar^2 B_o}{8 kT} \quad (12)$$

$$M_o = \frac{8 N \gamma^2 \hbar^2 B_o}{5 kT} + \frac{2 N \gamma^2 \hbar^2 B_o}{5 kT} = 2 \frac{N \gamma^2 \hbar^2 B_o}{kT} \quad (13)$$

For the spin 5/2 system the calculation is:

$$M_o = n_{+5/2} \mu_{+5/2} + n_{+3/2} \mu_{+3/2} + n_{+1/2} \mu_{+1/2} + n_{-1/2} \mu_{-1/2} + n_{-3/2} \mu_{-3/2} + n_{-5/2} \mu_{-5/2}$$

$$M_o = (n_{+5/2} - n_{-5/2}) \mu_{+5/2} + (n_{+3/2} - n_{-3/2}) \mu_{+3/2} + (n_{+1/2} - n_{-1/2}) \mu_{+1/2}$$

$$M_o = (n_{+5/2} - n_{-5/2}) \frac{5}{2} \gamma \hbar + (n_{+3/2} - n_{-3/2}) \frac{3}{2} \gamma \hbar + (n_{+1/2} - n_{-1/2}) \frac{1}{2} \gamma \hbar$$

$$M_o = \frac{5N \gamma \hbar B_o}{6 kT} \frac{5}{2} \gamma \hbar + \frac{3N \gamma \hbar B_o}{6 kT} \frac{3}{2} \gamma \hbar + \frac{N \gamma \hbar B_o}{6 kT} \frac{1}{2} \gamma \hbar = \left( \frac{25}{12} + \frac{9}{12} + \frac{1}{12} \right) \frac{N \gamma^2 \hbar^2 B_o}{kT}$$

has five energy levels (+2, +1, 0, -1,-2), the approximated population for each energy level is **N/5**. Accordingly, the energy difference for the compared energy levels are  $4\gamma \hbar B_o$ ,  $2\gamma \hbar B_o$  and 0 for the systems +2 with -2, +1 with -1 and 0 systems, respectively.

For these same systems the population differences are:

$$n_{+2} - n_{-2} = \frac{4 N \gamma \hbar B_o}{5 kT} \quad \text{and} \quad n_{+1} - n_{-1} = \frac{2 N \gamma \hbar B_o}{5 kT}$$

and because the respective magnetic moments are  $\mu_{+2} = 2\gamma \hbar$  and  $\mu_{+1} = \gamma \hbar$ , the final liquid magnetization expression is given by Equation 13.

$$M_o = \frac{35}{12} \frac{N\gamma^2\hbar^2 B_o}{kT} \quad (14)$$

At this point, if we make a table including all the characteristics for each spin system, we can prepare a general equation for  $M_o$ . Table 1 shows all the necessary data.

Accordingly, the general equation for  $M_o$  corresponds to Equation 15:

$$M_o = \sum_j^{\vartheta} \frac{(\Delta m_{ij})m_{ij}}{\Xi} \frac{N\gamma^2\hbar^2 B_o}{kT} \quad (15)$$

The value of  $\Delta m_{ij}$  corresponds to the difference between the  $m_i$  values of the energy levels with the same absolute value of  $m_i$  ( $|m_i|$ ). The number  $j$  corresponds to the number of  $\Delta m_i$  values for each system. The application of Equation 15 is very simple, as shown for the system with spin 3, in which  $\Xi$  corresponds to 7,  $\vartheta$  is 3, the  $\Delta m_i$  values are 6, 4 and 2, and the values of  $m_i$  are 3, 2 and 1, thus expressing  $M_o$  as:

$$M_o = \left( \frac{3 \times 6 + 2 \times 4 + 1 \times 2}{7} \right) \frac{N\gamma^2\hbar^2 B_o}{kT} = 4 \frac{N\gamma^2\hbar^2 B_o}{kT} \quad (\text{for spin 3})$$

**Table 1.** Numerical characteristics for the spin systems from  $1/2$  to  $5/2$ .

Spin	$m_i$ values	$\Xi$ (n° of $m_i$ values)	$\Delta m_i$	$\vartheta$ (n° of $\Delta m_i$ )
$1/2$	+1/2, -1/2	2	1	1
1	+1, 0, -1	3	2	1
$3/2$	+3/2, +1/2, -1/2, -3/2	4	1, 3	2
2	+2, +1, 0, -1, -2	5	2, 4	2
$5/2$	+5/2, +3/2, +1/2, -1/2, -3/2, -5/2	6	1, 6, 10	3

Finally, if we compare the coefficients of all the calculated  $M_o$  values, it is possible to construct Table 2, in which the results are compared.

Analyzing these results it is easy to see that the difference between the coefficients can be described by the general expression  $\frac{2\eta+3}{12}$ , where the number  $\eta$  corresponds to 1, 2, 3, 4..., and because the spin under examination would be described as  $\frac{\eta}{2}$  the coefficient

difference would be  $\frac{4I+3}{12}$ , where  $I$  is the nuclear spin ( $I=1/2, 1, 3/2, 2 \dots$ ).

Knowing that the coefficient for the  $M_o$  expression for spin  $1/2$  is  $3/12$ , the coefficient for any other spin system would be described by Equation 16 and the general expression for  $M_o$  for any spin system would be given by Equation 17.

$$\frac{3}{12} + \sum_I \frac{4I+3}{12} \quad (16)$$

$$M_o = \left[ \frac{3}{12} + \sum_I \frac{4I+3}{12} \right] \frac{N\gamma^2\hbar^2 B_o}{kT} \quad (17)$$

**Table 2.** Comparison between the values and coefficients of the expression of  $M_o$  for the spin systems of  $1/2$  to 3.

<b>Spin</b>	$1/2$	1	$3/2$	2	$5/2$	3
<b>Coefficient</b>	$1/4$	$2/3$	$5/4$	2	$35/12$	4
<b>Normalized coefficient</b>	$3/12$	$8/12$	$15/12$	$24/12$	$35/12$	$48/12$
<b>Coefficient difference</b>	--	$5/12$	$7/12$	$9/12$	$11/12$	$13/12$
<b><math>\eta</math></b>	1	2	3	4	5	6

Equation 17 shows that the liquid magnetization depends on the spin of the nuclear system under study and, in principle, the greater the nuclear spin value, the greater is the value of  $M_0$  and the NMR signal intensity.

This is an important result, as the value of the liquid magnetization is necessary to calculate the absolute and the relative intensity values of the different NMR signals, a process that is related to signal intensity manipulation using pulse sequences, as it will be discussed in the future articles of the "Understanding NMR Pulse Sequences" collection.

## References

1. Figueroa-Villar, J. D.; *Aspectos Quânticos da Ressonância Magnética Nuclear em Fundamentos e Aplicações da Ressonância Magnética Nuclear Vol. 2*, 2nd Edition, Figueroa-Villar, J. D. Editor, AUREMN, Rio de Janeiro, **2002**.
2. Figueroa-Villar, J. D. Understanding NMR Pulse Sequences. Part 1. Understanding Magnetic Excitation with the Semi-classical Vector Model. *Ann. Magn. Reson.* **2008**, 6, 1-16.