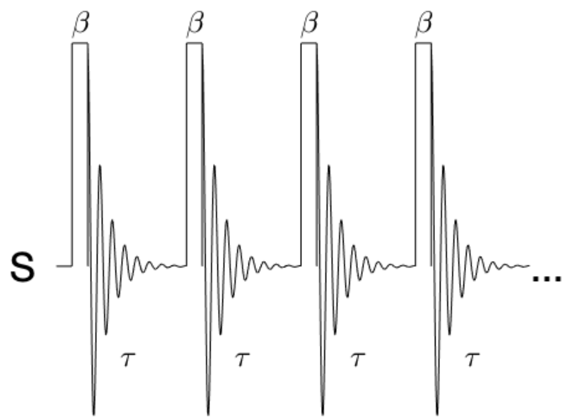
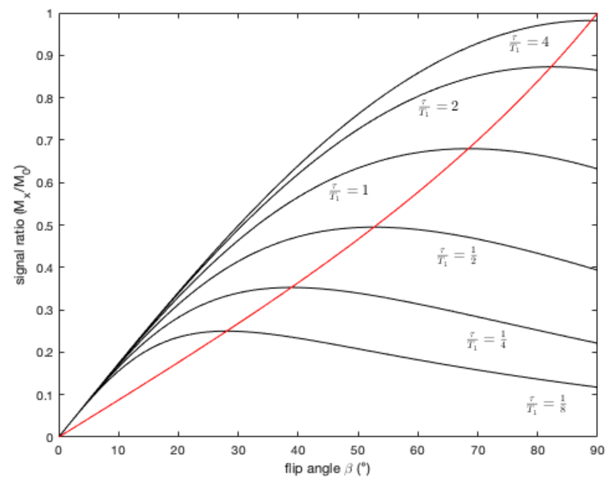
July 2022 NMR Topic of the Month: The Ernst Angle

How does one acquire the most signal in the least amount of time?

A more general phrasing of this question would be: how can one engineer a repetitive sequence of rf pulses to maximize the observed signal over time? This question was addressed very early with the introduction of pulsed NMR.





A first look at the solution.

The basic experiment in question is shown above on the left. It is a series of pulse-acquire experiments run back-to-back. If we first make some assumptions:

1. the transverse relaxation time $\left(T_2\right)$ is much, much less than the longitudinal relaxation time $\left(T_1\right)$
2. the pulse is on-resonance with the signal observed
3. the pulse length is very short compared to the time between pulses (τ)

Then the pseudo equilibrium of the experiment may easily be determined by matching the signal available just after an acquisition to that just following a pulse. Evaluating that condition leads to the following:

$$\frac{M_x}{M_0} = \frac{1-exp\left[-\tau/T_1\right]}{1-exp\left[-\tau/T_1\right]cos\beta} sin\beta$$

Where M_x is the transverse magnetization generated by the pulse, M_0 is the thermal equilibrium magnetization, τ is the acquisition time, and β is the pulse rotation (flip) angle. The maximum of this expression is found by setting the derivative of M_x/M_0 with respect to β to zero and solving for β, which yields $cos\beta_{opt} = exp\left[-\ \tau/T_1\right]$ (called the Ernst angle). Substituting back into the magnetization expression yields:

$$\left(\frac{M_x}{M_0}\right)_{opt} = \frac{sin\beta_{opt}}{1+cos\beta_{opt}}$$

The magnetization curves for various ratios of the time between pulses (τ) to the longitudinal relaxation time $\left(T_1\right)$ versus the flip angle are shown in black in the plot above on the right. The curve showing the magnetization versus optimum flip angle is shown in red in the plot above on the right, so where it intersects a given magnetization and τ/T_1curve is the maximum for that τ/T_1.

What about a liquid sample?

In a solid sample the first assumption above is likely to be true, but this is not the case in a liquid sample. However, it is always true that $T_2 \leq 2T_1$, often true that $T_2 \leq T_1$, and commonly approximated in a liquid that $T_2 \approx T_1$. Allowing the relaxation superoperator to be the traditional $\hat{\hat{\Gamma}} = \Lambda\left(exp\left[-\tau/T_2\right], exp\left[-\tau/T_2\right], exp\left[-\tau/T_1\right]\right)$, the magnetization following the pulses is:

$$\frac{M_x}{M_0} = \frac{\left(1-exp\left[-\tau/T_1\right]\right)\left(1-exp\left[-\tau/T_2\right]cos\vartheta\right)sin\beta}{\left(1-exp\left[-\tau/T_1\right]cos\beta\right)\left(1-exp\left[-\tau/T_2\right]cos\vartheta\right)-\left(exp\left[-\tau/T_1\right]-cos\beta\right)\left(exp\left[-\tau/T_2\right]-cos\vartheta\right)exp\left[-\tau/T_2\right]}$$

Where M_0 is the thermal equilibrium magnetization, ϑ is the (modulo 2π) free precession angle during τ, and β is the flip angle of the pulse. To get the maximum, again set the first derivative with respect to β to zero and solve for β.

$$\frac{d}{d\beta}\frac{M_x}{M_0} = \frac{\left(1-exp\left[-\tau/T_1\right]\right)\left(1-exp\left[-\tau/T_2\right]cos\vartheta\right)cos\beta}{\left(1-exp\left[-\tau/T_1\right]cos\beta\right)\left(1-exp\left[-\tau/T_2\right]cos\vartheta\right)-\left(exp\left[-\tau/T_1\right]-cos\alpha\right)\left(exp\left[-\tau/T_2\right]-cos\vartheta\right)exp\left[-\tau/T_2\right]}$$

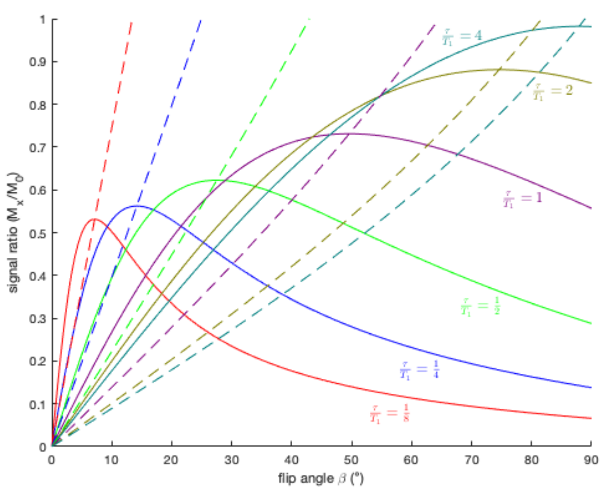
$$-\frac{\left(1-exp\left[-\tau/T_1\right]\right)\left(1-exp\left[-\tau/T_2\right]cos\vartheta\right)sin\alpha\left\{exp\left[-\tau/T_1\right]sin\beta\left(1-exp\left[-\tau/T_2\right]cos\vartheta\right)-sin\beta\left(exp\left[-\tau/T_2\right]cos\vartheta\right)exp\left[-\tau/T_2\right]\right\}}{\left\{\left(1-exp\left[-\tau/T_1\right]cos\beta\right)\left(1-exp\left[-\tau/T_2\right]cos\vartheta\right)-\left(exp\left[-\tau/T_1\right]-cos\beta\right)\left(exp\left[-\tau/T_2\right]-cos\vartheta\right)exp\left[-\tau/T_2\right]\right\}^2} = 0$$

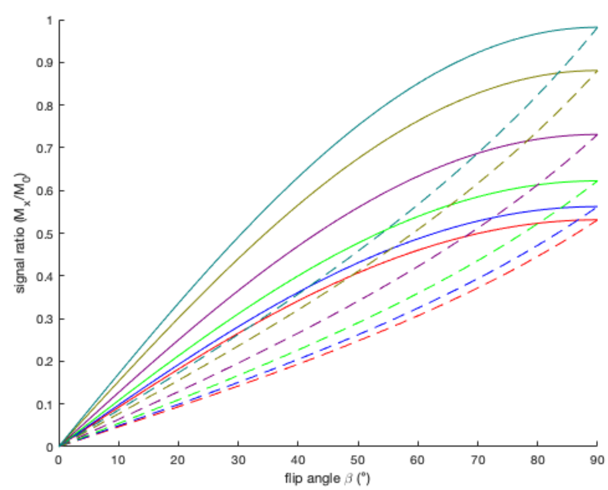
$$cos\beta_{opt} = \frac{exp\left[-\tau/T_1\right]+exp\left[-\tau/T_2\right]\left(cos\vartheta-exp\left[-\tau/T_2\right]\right)/\left(1-exp\left[-\tau/T_2\right]cos\vartheta\right)}{1+exp\left[-\tau/T_1\right]exp\left[-\tau/T_2\right]\left(cos\vartheta-exp\left[-\tau/T_2\right]\right)/\left(1-exp\left[-\tau/T_2\right]cos\vartheta\right)}$$

Then, as above, we substitute into the magnetization expression to determine the optimum value, which gives:

$$\left(\frac{M_x}{M_0}\right)_{opt} = \left(\frac{1-exp\left[-\tau/T_2\right]cos\vartheta}{1-2exp\left[-\tau/T_2\right]cos\vartheta+exp\left[-2\tau/T_2\right]}\right)\left(\frac{sin\beta_{opt}}{1+cos\beta_{opt}}\right)$$

Below on the left are the magnetization curves for $T_2 = T_1$ and $\vartheta = 0$, and below on the right are the magnetization curve for $T_2 = T_1$ and $\vartheta = \pi$ (the colors of the curves are consistent between the figures). As ϑ increases the magnetization curves very quickly morph from those shown on the left to those on the right; however, for small precession angles there is a dramatic effect on the magnetization. The larger the value of T_2/T_1, the smaller the optimum flip angles will be, but the more magnetization will be produced at those smaller flip angles.





References

1. R.R. Ernst and W.A. Anderson, *Rev. Sci. Instrum.* **37**(1), 93 (1966).
2. R.R. Ernst, G. Bodenhausen, and A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Oxford Science Publications, New York (1987) Chapter 4.2.