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Communication

Linking NMR pulse sequences: Derivative relation between the responses of two pulse sequences

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Abstract

Examples are shown of how the derivative of the response of an NMR pulse sequence with respect to a variable in that pulse sequence can be obtained by another pulse sequence. This approach holds the potential of being a tool for discovery of new pulse sequences or a means of understanding how some pulse sequences are related to each other.

Keywords: Pulse sequence derivative; APT; INEPT; SEMUT; DEPT

In NMR spin engineering a multitude of theoretical tools has been used to develop numerous pulse sequences. In fact, if not a concrete practical problem it is often a new tool or a variation of a known tool that has led to new experiments. Hence it is relevant to consider refinements of the theoretical framework or to search for new ways of analyzing manipulations to spin systems.

This paper takes a different approach. It is a step towards exploring links between NMR pulse sequences, i.e., an attempt to establish connections between pulse sequences. While this exercise at first glance might seem rather academic, it has potential practical implications, because possibly so far absent links will show up in the analysis and some of such pulse sequences could turn out to be useful. Although not related to the present work the literature contains for example a systematic way of deriving progressively better composite pulses [1] and decoupling schemes [2].

The response or detected signal after a pulse sequence can be a function of a variable in the pulse sequence (e.g., a flip angle or a delay), and the derivative of this response function with respect to the variable can be determined. Then the question is whether a pulse sequence can be designed whose response function is equal to the derivative of the first response function. That would then establish a link between the two pulse sequences, and if the second one can be derived systematically from the first one, the procedure represents a potentially useful tool for discovery of new pulse sequences. This paper will present a few examples of such links between pulse sequences.

The APT-type pulse sequences [3–5] were the first experiments for distinguishing or editing ^{13}C (the S spin) NMR spectra according to the number of attached protons (the I spins). The APT pulse sequence is shown in Fig. 1A and the detected signal can be represented in the following way where

$$F_\phi = \sum_{j=1}^{n} I_{j\phi}, \quad \phi = x, y, z, \tag{1}$$

$$\begin{aligned} M^{\mathrm{APT}} = \mathrm{Tr}\Big\{ & S_y \exp\left(-\mathrm{i}\pi J \frac{\tau}{2} 2F_z S_z\right) \exp\left(-\mathrm{i}\pi(F_x + S_x)\right) \\ & \times \exp\left(-\mathrm{i}\pi J \frac{\tau}{2} 2F_z S_z\right) \exp\left(-\mathrm{i}\frac{\pi}{2} S_x\right) S_z \\ & \times \exp\left(\mathrm{i}\frac{\pi}{2} S_x\right) \exp\left(\mathrm{i}\pi J \frac{\tau}{2} 2F_z S_z\right) \\ & \times \exp\left(\mathrm{i}\pi(F_x + S_x)\right)\left(\mathrm{i}\pi J \frac{\tau}{2} 2F_z S_z\right)\Big\}, \end{aligned} \tag{2}$$

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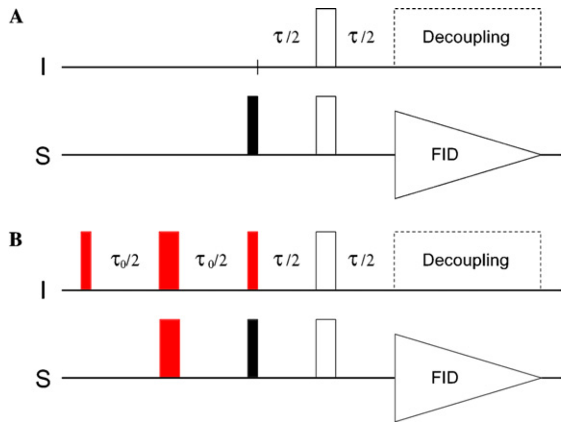

Fig. 1. Pulse sequences (A) APT [3–5] and (B) refocused INEPT [6,7]. Filled and open bars represent $\pi/2$ and π pulses, respectively. τ_0 is a fixed delay of $(2J)^{-1}$ while τ can be varied to determine S-spin (i.e., ^{13}C) multiplicities. The only critical phase setting is that the phases of the two I-spin $\pi/2$ pulses must be shifted with 90° with respect to each other.

$$= \mathrm{Tr}\left\{S_y \exp(-\mathrm{i}\pi J\tau 2F_zS_z)\exp\left(\mathrm{i}\frac{\pi}{2}S_x\right)S_z \times \exp\left(-\mathrm{i}\frac{\pi}{2}S_x\right)\exp(\mathrm{i}\pi J\tau 2F_zS_z)\right\}, \tag{3a}$$

$$= \mathrm{Tr}\left\{S_x \exp(-\mathrm{i}\pi J\tau 2F_zS_z)\exp\left(-\mathrm{i}\frac{\pi}{2}S_y\right)S_z \times \exp\left(\mathrm{i}\frac{\pi}{2}S_y\right)\exp(\mathrm{i}\pi J\tau 2F_zS_z)\right\}, \tag{3b}$$

$$= \mathrm{Tr}\{S_x \exp(-\mathrm{i}\pi J\tau 2F_zS_z)S_x \exp(\mathrm{i}\pi J\tau 2F_zS_z)\}, \tag{4}$$

$$= \cos^n(\pi J\tau). \tag{5}$$

Eq. (4) is a convenient form for forming the derivative

$$\frac{\mathrm{d}M^{\mathrm{APT}}}{\mathrm{d}(\pi J\tau)} = \mathrm{Tr}\{-\mathrm{i}S_x \exp(-\mathrm{i}\pi J\tau 2F_zS_z)[2F_zS_z, S_x] \times \exp(\mathrm{i}\pi J\tau 2F_zS_z)\}$$
$$= -\,\mathrm{Tr}\left\{-S_x \exp(-\mathrm{i}\pi J\tau 2F_zS_z)\exp\left(\mathrm{i}\frac{\pi}{2}S_x\right) \times \{2F_zS_z\}\exp\left(-\mathrm{i}\frac{\pi}{2}S_x\right) \times \exp(\mathrm{i}\pi J\tau 2F_zS_z)\right\}, \tag{6}$$
$$= -\,n\sin(\pi J\tau)\cos^{n-1}(\pi J\tau). \tag{7}$$

Comparison between Eqs. (3a) and (6) along with Eqs. (5) and (7) show that the derivative of the response of the APT pulse sequence apart from a $\pi/2$ phase shift is obtained by applying that same pulse sequence to the initial state $-2F_zS_z$, which in turn apart from a proportionality factor is obtained by applying a bilinear $\pi J\tau 2F_yS_z$ and a $-(\pi/2)F_y$ rotation to F_z. The resulting pulse sequence is shown in Fig. 1B and it is obvious that what in this sense turns up as the derivative for the APT pulse sequence is refocused INEPT [6,7].

A slightly more challenging example of a pulse sequence response derivative is the next higher level of

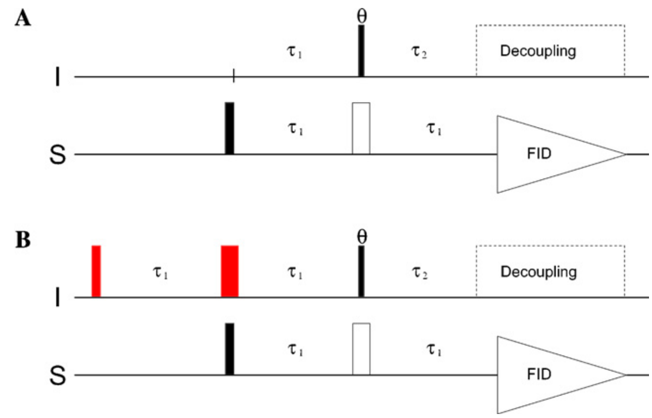

Fig. 2. Pulse sequences (A) SEMUT [8] and (B) DEPT [9]. Filled and open bars represent $\pi/2$ and π pulses, respectively. τ_1 and τ_2 are delays on the order of $(2J)^{-1}$ adjusted to the applicable J range. The I-spin flip angle θ can be varied to result in S-spin spectra edited according to S-spin (i.e., ^{13}C) multiplicities. The only critical phase setting is that the phases of the two I-spin pulses of flip angle $\pi/2$ and θ, respectively, must be shifted with 90° with respect to each other.

^{13}C editing accuracy above APT, namely SEMUT [8], the pulse sequence of which is outlined in Fig. 2A.

$$M^{\mathrm{SEMUT}} = \mathrm{Tr}\{S_y \exp(-\mathrm{i}\pi J\tau_2 2F_zS_z)\exp(-\mathrm{i}\theta F_y) \times \exp(-\mathrm{i}\pi S_x)\exp(-\mathrm{i}\pi J\tau_1 2F_zS_z) \times \exp\left(-\mathrm{i}\frac{\pi}{2}S_x\right)S_z\exp\left(\mathrm{i}\frac{\pi}{2}S_x\right) \times \exp(\mathrm{i}\pi J\tau_1 2F_zS_z)\exp(\mathrm{i}\pi S_x) \times \exp(\mathrm{i}\theta F_y)\exp(\mathrm{i}\pi J\tau_2 2F_zS_z)\}, \tag{8}$$

$$= \mathrm{Tr}\{S_y \exp(-\mathrm{i}\pi J\tau_2 2F_zS_z)\exp(-\mathrm{i}\theta F_y) \times \exp(\mathrm{i}\pi J\tau_1 2F_zS_z)\exp\left(\mathrm{i}\frac{\pi}{2}S_x\right)S_z\exp\left(-\mathrm{i}\frac{\pi}{2}S_x\right) \times \exp(-\mathrm{i}\pi J\tau_1 2F_zS_z)\exp(\mathrm{i}\theta F_y) \times \exp(\mathrm{i}\pi J\tau_2 2F_zS_z)\}, \tag{9}$$

$$= \mathrm{Tr}\{S_y \exp(-\mathrm{i}\pi J\tau_2 2F_zS_z)\exp(-\mathrm{i}\theta F_y) \times \exp(\mathrm{i}\pi J\tau_1 2F_zS_z)S_y\exp(-\mathrm{i}\pi J\tau_1 2F_zS_z) \times \exp(\mathrm{i}\theta F_y)\exp(\mathrm{i}\pi J\tau_2 2F_zS_z)\}, \tag{10a}$$

$$= \mathrm{Tr}\{S_x \exp(-\mathrm{i}\pi J\tau_2 2F_zS_z)\exp(-\mathrm{i}\theta F_y) \times \exp(\mathrm{i}\pi J\tau_1 2F_zS_z)S_x\exp(-\mathrm{i}\pi J\tau_1 2F_zS_z) \times \exp(\mathrm{i}\theta F_y)\exp(\mathrm{i}\pi J\tau_2 2F_zS_z)\}, \tag{10b}$$

$$\frac{dM^{\mathrm{SEMUT}}}{\mathrm{d}\theta} = \mathrm{Tr}\{-\mathrm{i}S_x \exp(-\mathrm{i}\pi J\tau_2 2F_zS_z)\exp(-\mathrm{i}\theta F_y) \times [F_y, \exp(\mathrm{i}\pi J\tau_1 2F_zS_z)S_x\exp(-\mathrm{i}\pi J\tau_1 2F_zS_z)] \times \exp(\mathrm{i}\theta F_y)\exp(\mathrm{i}\pi J\tau_2 2F_zS_z)\}$$
$$= \mathrm{Tr}\{-\mathrm{i}S_x \exp(-\mathrm{i}\pi J\tau_2 2F_zS_z)\exp(-\mathrm{i}\theta F_y) \times \exp(\mathrm{i}\pi J\tau_1 2F_zS_z)\exp\left(\mathrm{i}\frac{\pi}{2}S_x\right) \times [\exp(\mathrm{i}\pi J\tau_1 2F_zS_y)F_y\exp(-\mathrm{i}\pi J\tau_1 2F_zS_y), S_x] \times \exp\left(-\mathrm{i}\frac{\pi}{2}S_x\right)\exp(-\mathrm{i}\pi J\tau_1 2F_zS_z) \times \exp(\mathrm{i}\theta F_y)\exp(\mathrm{i}\pi J\tau_2 2F_zS_z)\}$$

$$
\begin{aligned}
=\mathrm{Tr}\{&-S_x \exp(-\mathrm{i}\pi J\tau_2 2F_zS_z)\exp(-\mathrm{i}\theta F_y)\\
&\times \exp(\mathrm{i}\pi J\tau_1 2F_zS_z)\exp\left(\mathrm{i}\frac{\pi}{2}S_x\right)\\
&\times \{\sin(\pi J\tau_1)2F_xS_z\}\exp\left(-\mathrm{i}\frac{\pi}{2}S_x\right)\\
&\times \exp(-\mathrm{i}\pi J\tau_1 2F_zS_z)\exp(\mathrm{i}\theta F_y)\\
&\times \exp(\mathrm{i}\pi J\tau_2 2F_zS_z)\}. \qquad (11)
\end{aligned}
$$

In analogy to the preceding example, the derivative of the SEMUT response can be produced by that same pulse sequence starting with another initial state, $-\sin(\pi J\tau_1)2F_yS_z$. The full pulse sequence producing the SEMUT derivative is DEPT [9] outlined in Fig. 2B. The derivative relation also exists between the SEMUT GL and DEPT GL pulse sequences suppressing J cross-talk over wide ranges of coupling constants [10–12].

Since the early days of ^{13}C editing it has been known that the editing accuracy or susceptibility to J cross-talk is identical for, e.g., SEMUT and DEPT [8], which also follows from the derivative relationship.

In conclusion, this paper has touched on a new approach of exploring "derivatives of pulse sequences" in order to establish links between NMR experiments. It was shown that the derivative with respect to a delay involving J evolution to a passive spin leads to a sequence including polarization transfer from that spin appended to the original pulse sequence. Likewise, the derivative with respect to a flip angle applied to passive spins in a state of antiphase with respect to an active spin also leads to a pulse sequence with polarization transfer from these passive spins and again with the original sequence appended.

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