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# Determination of NMR cogwheel phase cycle with XML

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ABSTRACT

The selection of correct coherence transfer pathways is an essential component of an NMR pulse sequence. This article describes a new method based on the use of web tools (eXtensible Markup Language and eXtensible Stylesheet Language Transformation) to generate a cogwheel phase cycle for selecting coherence transfer pathways. We illustrate this method with the three-pulse phase-modulated shifted-echo or split-$t_1$ MQMAS sequences for triple-quantum spin-3/2 systems. After generalization to the different half-integer quadrupole spins, we use the SIMPSON program to confirm our results. Finally, we apply our method to the case of the *z*-filter 3QMAS sequence for $I = 3/2$ systems.


## 1. Introduction

The choice of coherence transfer pathways is vital in solid- and liquid-state NMR pulse sequences. To achieve this, two main methods are commonly used: pulsed field gradient [1–3] and phase cycling. They allow not only the selection of the desired signal but also the suppression of uninteresting NMR signals or artefacts arising from instrumental imperfections. The first method for phase cycling construction is the classical "nested" phase cycling proposed by Bodenhausen et al. [4] and by Bain [5], where the phase of each RF block is cycled separately while the phases of the other RF blocks are kept constant. To reduce the experiment time, we often try to build a phase cycle of minimal length. Some workers have investigated the possibility of generating shorter phase cycles [6–8]. Recently Levitt et al. proposed two new approaches: cogwheel phase cycling [9] and multiplex phase cycling [10]. In multiplex phase cycling, data are recorded after some phase increment instead of at the end of a complete cycle. Malicki et al. [11] applied this phase cycling to the MQMAS method. Moreover, we have proposed a procedure to optimize the pulse durations for recording multiplex $\pm 3Q$ and $\pm 5Q$ MAS experiments within the same data acquisition [12]. This method is based on the simulation of the echo and the anti-echo amplitudes of a spin *I* with increasing pulse durations in a powder rotating at the magic angle, using Mathematica [13] and SIMPSON [14]. In cogwheel phase cycling, the phases of all the RF blocks are incremented simultaneously. In many cases, use of the cogwheel concept reduces the minimum number of steps in the phase cycle [9,15–18]. It is also used with success in multidimensional liquid-state NMR experiments [19,20]. However, the determination of various parameters involved in cogwheel phase cycling requires a numerical search. In the literature, there are few methods for making this search. Jerschow and Kumar propose a C# program [15,21].

In this paper, we present a procedure using two web tools [22]: XML (eXtensible Markup Language [23–25]) for modelling pulse sequences and cogwheel phase cycling and XSLT (eXtensible Stylesheet Language Transformation [26,27]) for the numerical search of cogwheel parameters. After a short description of cogwheel phase cycling, we introduce the two web tools: XML and XSLT. We illustrate our method by applying it to phase-modulated shifted-echo [28] or split-$t_1$ [29] +3QMAS sequences for spin-3/2 systems. The phases cycling of the three pulses and of the receiver are identical for the two sequences; only the division of spin evolution times is different. They allow recording the whole echo or anti-echo during the acquisition time, but in the case of split-$t_1$, the echo appears at a fixed position in the $t_2$ time domain. We consider the case where the pulses have the same amplitude but the result remains valid for a third pulse of weak amplitude. We show that our results are identical with those found by Levitt et al. [9], Goldbourt and Madhu [30] and Jerschow and Kumar [15] via transformations. We discuss its generalization to four half-integer quadrupole spins like Goldbourt and Madhu

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[30]. We suggest using the SIMPSON program to confirm our results. Details of this procedure are available in our website: www.pascal-man.com. We use our method for determining the cogwheel phase cycle associated with the selection of the echo and anti-echo transfer pathways of a spin $I=3/2$ systems with $z$-filter sequence [31].

## 2. Cogwheel phase cycling

This presentation is adapted from that of Levitt et al. [9]. Consider a pulse sequence composed of $M$ independent blocks $B_i$ $(1\leqslant i\leqslant M)$. The signal $S(p)$ from a general coherence transfer pathway $p=\{0Q\rightarrow p_{B_1B_2}Q\rightarrow\cdots\rightarrow p_{B_{M-1}B_M}Q\rightarrow -1Q\}$ after $N$ steps of phase cycling is given by [32]

$$S(p)=\frac{1}{N}\sum_{m=0}^{N-1}\exp\{-i\phi^{(m)}(p)\},\tag{1}$$

where $\phi^{(m)}$ is the pathway phase for transient $m$. In cogwheel phase cycling, the phases of the pulse sequence blocks and the receiver are incremented simultaneously as

$$\phi_{B_1}^{(m)}=\frac{2\pi W_{B_1}}{N}m,\quad \phi_{B_2}^{(m)}=\frac{2\pi W_{B_2}}{N}m,\ldots,$$
$$\phi_{B_M}^{(m)}=\frac{2\pi W_{B_M}}{N}m,\quad \phi_{rec}^{(m)}=\frac{2\pi W_{rec}}{N}m,\tag{2}$$

where $W_{B_i}$ is an integer, called the winding number of block $B_i$ and $W_{rec}$ the receiver winding number. The pathway phase can be expressed by [9]

$$\phi^{(m)}(p)=\frac{2\pi m}{N}[(W_{B_1}-W_{B_2})p_{B_1B_2}+(W_{B_2}-W_{B_3})p_{B_2B_3}+\cdots + (W_{B_{M-1}}-W_{B_M})p_{B_{M-1}B_M}-W_{B_M}]+\phi_{rec}^{(m)}.\tag{3}$$

Generally, the set of $N$ phase cycling experiments allows us to add the signals from desired pathways constructively and those from undesired pathways destructively [32]. In this case, the pathway phase must satisfy the condition:

$$\phi^{(m)}(p)\begin{cases}=2\pi R & \text{if } p\in\{p^0,p^1,\ldots\}\\ \neq 2\pi R & \text{otherwise,}\end{cases}\tag{4}$$

where $R$ is an integer and $p^0,p^1,\ldots$ are the desired coherence transfer pathways. From this condition, the receiver phase for transient $m$ is adjusted to select a desired pathway. For example, for $p^0$ it is defined by

$$\phi^{(m)}(p^0)=0.\tag{5}$$

In this case

$$\phi_{rec}^{(m)}=-\frac{2\pi m}{N}[(W_{B_1}-W_{B_2})p^0_{B_1B_2}+(W_{B_2}-W_{B_3})p^0_{B_2B_3}+\cdots + (W_{B_{M-1}}-W_{B_M})p^0_{B_{M-1}B_M}-W_{B_M}],\tag{6}$$

and Eq. (3) can be expressed as

$$\phi^{(m)}(p)=\frac{2\pi m}{N}[(W_{B_1}-W_{B_2})(p_{B_1B_2}-p^0_{B_1B_2}) + (W_{B_2}-W_{B_3})(p_{B_2B_3}-p^0_{B_2B_3})+\cdots + (W_{B_{M-1}}-W_{B_M})(p_{B_{M-1}B_M}-p^0_{B_{M-1}B_M})].\tag{7}$$

The signal $S(p)$ is not zero if the condition in Eq. (4) is fulfilled, that is

$$(W_{B_2}-W_{B_1})(p_{B_1B_2}-p^0_{B_1B_2})+\cdots+(W_{B_M}-W_{B_{M-1}})(p_{B_{M-1}B_M}-p^0_{B_{M-1}B_M}) = N\times\text{integer}.\tag{8}$$

It is equivalent to

$$\sum_{i=1}^{M-1}(W_{B_{i+1}}-W_{B_i})(p_{B_iB_{i+1}}-p^0_{B_iB_{i+1}})\bmod N=0,\tag{9}$$

where mod is the modulus operator. There are as many conditions in Eq. (9) as the number of desired coherence transfer pathways. It is very important to note that these conditions are satisfied not only by the desired coherence transfer pathways but also by other unwanted pathways.

The main difficulty about cogwheel phase cycling is the numerical search for the number of steps $N$ and the winding numbers. Fortunately, we can use rules established by Hughes et al. [16] to estimate the minimum $N$ value. To determine the winding numbers of a specific coherence transfer pathway, it is necessary to consider all the pathways for a spin $I$. Indeed, the number of possible coherence orders between two neighbouring RF blocks is $(4I+1)$, and for each of them the winding number can take any value between 1 and $N-1$. We obtain a tree structure which quickly becomes complex. We found this tree diagram in structured documents for data exchange on the web. We decided to use the web tools: XML and XSLT, which are adapted to this kind of problem and give the results simply. They have the advantage of being free of copyright, independent of the platform and their supports are significant and increasing.

After the determination of the winding numbers for the pulses with Eq. (9), the general equation of the receiver phase for transient $m$ [32]:

$$\phi_{rec}^{(m)}=-\sum_{i=1}^{M}\Delta p_{B_i}\phi_{B_i}^{(m)}\tag{10}$$

is used for determining the receiver winding number $W_{rec}$ (Eq. (2)).

There are as many relations in Eq. (10) as the number of desired coherence transfer pathways. Moreover, for some spectrometers, the receiver phase increment must be a multiple of $\pi/2$ and all phases involved in the pulse sequence must be positive. Fortunately, it is possible to manipulate the winding numbers and the phases. For this, we introduce three rules.

### 2.1. *First rule: one desired pathway is necessary for the determination of receiver winding number*

If several desired transfer pathways are involved in the sequence, it is sufficient to derive the receiver winding number with one desired transfer pathway. For example, we consider that two desired pathways $p^0$ and $p^1$ are selected. According to Eq. (6) the difference between receiver phases for the two pathways, $\phi_{rec}^{0,(m)}$ and $\phi_{rec}^{1,(m)}$ are

$$\phi_{rec}^{0,(m)}-\phi_{rec}^{1,(m)}=-\frac{2\pi m}{N}\sum_{i=1}^{M-1}(W_{B_{i+1}}-W_{B_i})(p^1_{B_iB_{i+1}}-p^0_{B_iB_{i+1}}).\tag{11}$$

Since Eq. (9) is valid for any general coherence transfer pathway $p$, it is also valid for the desired pathway $p^1$, that is

$$\sum_{i=1}^{M-1}(W_{B_{i+1}}-W_{B_i})(p^1_{B_iB_{i+1}}-p^0_{B_iB_{i+1}})\bmod N=0.\tag{12}$$

From Eq. (12) we deduce that the difference $\phi_{rec}^{0,(m)}-\phi_{rec}^{1,(m)}$ in Eq. (11) is a multiple of $2\pi$. In other words, $\phi_{rec}^{0,(m)}=\phi_{rec}^{1,(m)}$ in the $[0,2\pi[$ range and the receiver winding number $W_{rec}$ can be deduced from any desired pathway.

### 2.2. *Second rule: add the same integer to all winding numbers does not change the cogwheel phase cycling*

Ivchenko et al. [17] propose that the winding number of the receiver can be subtracted from all the winding numbers in the case of a perfect quadrature receiver. Indeed, the