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An analysis of the magic echo and solid echo sequence for quadrupolar echo spectroscopy of spin I=1 nuclei by average Hamiltonian theory

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Abstract. This work focuses on analyzing the dynamics of spin I=1 nuclei evolving under a simple two pulse echo cycle and a magic echo cycle by average Hamiltonian theory. The work highlights how spectral artifacts introduced by finite pulse widths can be removed by cycling the phases of the receiver and transmitter in a well defined way. In addition, it is shown that a magic echo cycle can refocus both the quadrupolar interaction together with any offset Hamiltonian. Due to higher convergence in the Magnus expansion magic echo based quadrupolar echo spectroscopy outperforms the conventional two pulse echo sequence.

Keywords: Quadrupolar Echo, Deuterium NMR, Solid Echo, Magic Echo

PACS: 82.33.Pt, 61.18.Fs, 82.56.Ub

INTRODUCTION

This work focuses on investigating the effects of finite pulse width artifacts and improving the signal to noise in spin-1 quadrupolar echo spectroscopy. To suppress the artifacts introduced from the ring down of the RF coil, a spin echo is applied in this technique for studying the broad quadrupolar spectra of a solid spin system. The method involves acquiring the peak of an echo, which under ideal experimental conditions and no relaxation, would yield a signal precisely equal to that of the free induction decay of a single pulse [1]. This scheme has been applied with great success for understanding various properties such as the orientation and rate of rotation of molecules of a broad range of polymer, solid and semisolid systems.

The signal acquired by a spin echo, however, is never free of instrumental artifacts often making interpretation of data challenging. A variety of techniques have been introduced to alleviate distortions commonly encountered in echo spectroscopy of spin-1 nuclei including phase cycling schemes for suppressing pulse transients and imperfect $\pi/2$ pulses, co-adding spectra acquired with different pulse spacings, or adding a two dimensional Fourier transform for removing feed-through signals and using composite pulses or chirped pulses for alleviating pulse power issues. An additional artifact often encountered causes an asymmetry of the spectra due to the evolution of the spin system under the quadrupolar Hamiltonian during the RF pulses. The work reports on a method for removing this asymmetry by cycling the phases of the receiver and transmitter. We also studied the application of magic echoes for improved quadrupolar echo spectroscopy. The magic echo cycle, developed by W-K. Rhim et. al. [2] nearly thirty six years ago, has been applied with great success in solid state NMR imaging, scattering.
studies and in multiple pulse line-narrowing schemes. A useful aspect of the cycles presented is their ability to refocus offset Hamiltonians simultaneously with the quadrupolar interaction. In addition, the signal to noise over the entire bandwidth is enhanced in a magic echo cycle compared to the familiar two pulse quadrupolar echo cycle due to more efficient convergence of the Magnus expansion with sufficient RF power.

THEORY

We analyze the spin dynamics of spin-1 nuclei evolving under the first order secular quadrupolar interaction subject to a large, static and homogeneous field and either the two pulse conventional quadrupolar echo sequence or the magic echo sequence. We assume that the quadrupolar interaction is significantly larger than any heteronuclear and homonuclear dipole interactions as well as any resonance offset present and that the system of interest is non-metallic, so that any paramagnetic shift anisotropy can be ignored. The cycle is known to refocus the time evolution of spin-1 nuclei evolving under the first order secular quadrupolar interaction which is given by

\[
H_{\omega Q} = \omega_Q R_{2,0} \frac{1}{\sqrt{6}} [12l_{z,1}l_{z,1} - II]
\]

In the above expression \( R_{2,0} = \sqrt{\frac{3}{2}} [P_2(cos(\theta)) + (\frac{1}{2})cos(2\theta)sin^2(\varphi)], P_2(cos(\theta)) \) is the second order Legendre polynomial of \( cos(\theta) \), \( \theta \) and \( \varphi \) are two of the three Euler angles and \( \omega'_Q = \frac{e^2 q Q}{2I(I-1)\hbar} \). The Hamiltonian has been written using the spin-1 operator formalism of S. Vega and A. Pines [3]. An illuminating approach for studying the dynamics of a spin system subject to an RF perturbation, given by J. S. Waugh and co-workers [4], is to consider the average or effective Hamiltonian of the RF pulse train. In this formalism, the time evolution of the system from time \( t=0 \), \( \rho(0) \) to the state at time \( t = t_c \), \( \rho(t_c) \) is given by

\[
\rho(t_c) = U_{RF} U_{int} \rho(0) U_{int}^{-1} U_{RF}^{-1}
\]

where the propagator \( U_{RF} \) is given by the Dyson series and \( U_{int} \) is given by the Magnus expansion. In the above, \( U_{RF} \) represents the interaction associated with the sequence of RF pulses applied over a time \( t_c \), and \( H_{int} \) refers to the systems’ internal Hamiltonian. An attractive feature of average Hamiltonian theory is that a variety of Hamiltonians can be accounted for in the system evolution including pulse errors and finite pulse width effects.

For conciseness we rewrote the quadrupolar Hamiltonian given in Eq. (1) more compactly as

\[
H_{\omega Q} = \omega_Q [12l_{z,1}l_{z,1} - II]
\]

where \( \omega_Q = \omega'_Q R_{2,0} \frac{1}{\sqrt{6}} \), and take the initial state of the system to be given by \( \rho(0) = I_{z,1} \).

The result of the zeroth order term of the Magnus expansion for the two pulse solid echo sequence is found to be

\[
\tilde{H}_{\omega Q}^0 = \frac{4\alpha \omega_Q}{\pi \tau} [I_{x,2} - I_{z,2}]
\]
and for the magic echo we find

\[
\mathcal{H}^0_{\omega Q} = \frac{1}{7\tau} \frac{12\alpha\omega_Q}{\pi} I_{x,2} + \frac{4(3\alpha - \tau)}{7\tau} \omega_Q [I_{x,1} I_{x,1} + I_{y,1} I_{y,1} - 2I_{z,1} I_{z,1}]
\]

(5)

The first order terms of the Magnus expansion are computed as follows.

\[
\mathcal{H}^1_{\text{int}}(ME) = \frac{1}{7\tau} \frac{\omega_Q^2}{\omega_{RF}^2} \left[ 18\sqrt{2} \frac{\pi}{8} I_{y,1} - \frac{9}{16}(4\sqrt{2} + (-2 + \sqrt{2}))I_{x,1} \right]
\]

(6)

\[
\mathcal{H}^1_{\text{int}}(SE) = \frac{B}{3\tau} I_{y,1} - \frac{A}{3\tau} I_{z,1} + \frac{A}{3\tau} I_{x,1}
\]

(7)

where

\[
A = \frac{18\alpha^2 \omega_Q^2}{\pi^2} \left[ \pi(-2 + \sin\left(\frac{\pi \tau}{2\alpha}\right)) + \sin\left(\frac{\pi \tau}{\alpha}\right) \right]
\]

(8)

and

\[
B = \frac{18\alpha^2 \omega_Q^2}{\pi^2} \left[ 1 + \cos\left(\frac{\pi \tau}{2\alpha}\right) \right]
\]

(9)

Setting the cycle time, \(7\tau\), of the magic echo cycle equal to that of the conventional two pulse cycle, \(3\tau\), the zeroth order term of the Magnus expansion for a magic echo given is the same magnitude as that given in the expression above. However, the zeroth order term of the Magnus expansion for the conventional cycle contains a sum of two terms, \(I_{x,2} - I_{x,2}\), whereas that of the magic echo only contains one which does not commute with the equilibrium state, \(I_{z,1}\). Hence, the dynamics are more complex for a given value of the pulse width, \(2\alpha\), for the conventional two pulse cycle. In addition, the first order term of the Magnus expansion for a magic echo is much smaller than that of the two pulse conventional cycle. A unique feature of the magic echo sequence is its ability in refocusing offset Hamiltonians together with the quadrupolar coupling. Following the formalism described above, the first order term of the Magnus expansion for the offset Hamiltonian for the magic echo is

\[
\mathcal{H}^0_{\Delta \omega}(ME) = -\frac{4}{7\tau} \frac{\Delta \omega}{\omega_{RF}} I_{x,1} + \frac{2}{7\tau} \frac{\Delta \omega}{\omega_{RF}} I_{x,1}
\]

\[
+ \frac{2}{7\tau} \frac{\Delta \omega}{\omega_{RF}} \left[ \omega_{RF}(\tau - 2\alpha) + 2\cos[\omega_{RF}(2\tau - \alpha)] - 1 \right] I_{z,1}
\]

(10)

where we have used the following constraints

\[
2\omega_{RF} \alpha = \frac{\pi}{2}
\]

(11)

and

\[
(2\tau - \alpha)\omega_{RF} = n\pi,
\]

\[n = 1, 2, 3, \ldots\]

(12)
For the solid echo cycle the zeroth order term for the chemical shift or static field inhomogeneity is

$$H_{\Delta \omega}^0(\text{SE}) = \frac{1}{3\tau}[-al_{x,1} + bl_{y,1} + al_{z,1}]$$  \hspace{1cm} (13)$$

where

$$a = 2\Delta \omega \left(\frac{4}{\pi} - 1\right)\alpha + \tau$$

$$b = 2\Delta \omega \left[2\left(\frac{4}{\pi} - 1\right)\alpha + \tau\right]$$  \hspace{1cm} (14)$$

In case where the $\omega_{RF}$ is made larger than $\Delta \omega$ the zeroth-order term of the Magnus expansion for the offset Hamiltonian with the magic echo sequence can be made negligible. In this situation the magic echo pulse sequence refocuses static field inhomogeneity and chemical shift effects completely. This is not the case with the conventional two pulse sequence and as a consequence it does not refocus the effects of static field inhomogeneity and chemical shift even for strong RF pulses. In reference [5] we show that by cycling the phases of the receiver as follows

$$\phi_1 = \{x, x, -x, -x, y, y, -y, -y\}$$

$$\phi_2 = \{y, -y, y, -y, x, -x, x, -x\}$$

$$RP = \{270, 270, 90, 90, 0, 0, 180, 180\}$$  \hspace{1cm} (15)$$

that the effects of finite pulse widths can be suppressed for the two pulse sequence. For the magic echo sequence a more complex phase cycling scheme is required and is given in reference [6]. The enhanced signal to noise using a magic echo and the ability to refocus an offset Hamiltonian more efficiently than the conventional two pulse cycle is demonstrated in reference [6].

**REFERENCES**