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Solid State Nuclear Magnetic Resonance
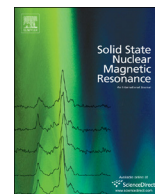
Effects of experimental imperfections on a spin counting experiment

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ABSTRACT

Spin counting NMR is an experimental technique that allows a determination of the size and time evolution of networks of dipolar coupled nuclear spins. This work reports on an average Hamiltonian treatment of two spin counting sequences and compares the efficiency of the two cycles in the presence of flip errors, RF inhomogeneity, phase transients, phase errors, and offset interactions commonly present in NMR experiments. Simulations on small quantum systems performed using the two cycles reveal the effects of pulse imperfections on the resulting multiple quantum spectra, in qualitative agreement with the average Hamiltonian calculations. Experimental results on adamantane are presented, demonstrating differences in the two sequences in the presence of pulse errors.

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1. Introduction

The free induction decay of an ensemble of dipolar-coupled spin-1/2 nuclei corresponds to the evolution of a single-spin, single-quantum state into multiple-spin, single-quantum terms. These multiple spin correlations are not directly detected in NMR experiments, however spin counting NMR [1] allows one to monitor their complex time evolution under a modified dipolar Hamiltonian. This modified dipolar Hamiltonian is applied using a well-defined pulse sequence. Because of its ability to measure the number of coupled spins in a dipolar coupled network, the spin counting method has been used to determine the effective spin cluster size in a variety of materials including polycrystalline samples [2], liquid crystals [3], and films [4]. The methodology has more recently been extended to study spin dynamics in quasi-1D spin chains [5] and cubic single crystals [6,7]. In the case of quasi-1D spin chains these pulse sequences are also used to monitor magnetization transport [8]. These techniques and their results have been used for theoretical studies of many-body spin dynamics [9,10] and to probe decoherence [11,12], i.e. for quantum computing. The decoherence experiments also implicitly probe the time-reversal properties of the pulse sequence, and understanding their sensitivity to errors may lead to improvements in their efficacy.

The aim of this work is to evaluate the contribution of pulse errors to the eight-pulse sequences shown in Fig. 1b and c, which are commonly used in multiple quantum spin-counting NMR. Since the experiments involve repeating either of these two pulse sequences many times, even small imperfections in the RF pulse

sequence may lead to large deviations from the ideal Hamiltonians —these errors can destroy the resulting quality of the multiple quantum spectra. Because of the use of these pulse sequences to encode thousands of spins [11] or more, eventually intrinsic limitations due to pulse errors should become important. In the section that follows we provide a brief overview of average Hamiltonian theory [13] which will be used to help quantify the effects of pulse errors. In Section 3 we present the results obtained from average Hamiltonian theory for the two sequences, as well as results of simulations and experiments which support the analytical results.

As a 2D sequence the multiple quantum NMR experiment can be separated into preparation, evolution, mixing, and detection periods (see also Fig. 1a). During the preparation period, under ideal conditions, the nuclear spins become correlated by evolving the system under an average (double quantum) Hamiltonian (in units of rad/s)

$$\overline{H}_D^0 = -\frac{1}{2} \sum_{j<k} \omega_D (I_j^+ I_k^+ - I_j^- I_k^-) \tag{1}$$

where ω_D is the dipolar coupling strength given by

$$\omega_D = \frac{\mu_0 \hbar \gamma^2}{8\pi r_{jk}^3} (1 - 3\cos^2\theta_{jk}). \tag{2}$$

In the above equation, r_{jk} is the internuclear distance and θ_{jk} is the angle between the vector r_{jk} and the external magnetic field B_0 [14]. Multiple quantum coherences created during the preparation period are transformed into an observable single quantum operator during the mixing period by applying a pulse sequence whose average Hamiltonian is the negative of Eq. (1), i.e.

$$\overline{H}_{D,m}^{(0)} = \frac{1}{2} \sum_{j<k} \omega_D (I_j^+ I_k^+ - I_j^- I_k^-). \tag{3}$$

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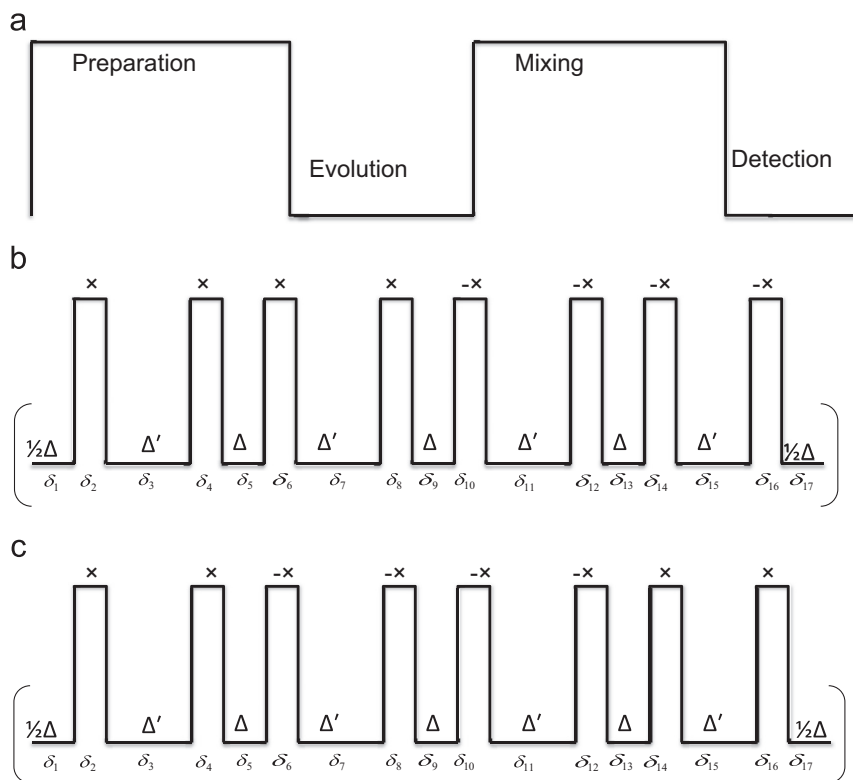E-mail address: gboutis@brooklyn.cuny.edu (G.S. Boutis).

Fig. 1. (a) The spin counting NMR experiment as a 2D experiment can be divided into four periods (preparation, evolution, mixing, and detection). Multiple-quantum coherences are built up during the preparation period. The total preparation period is generated by repeating the RF pulse sequence shown in (b) or (c) m times. The RF pulse cycle of the preparation period consists of eight $\pi/2$ pulses along the x-axis with widths $t_w = 2\alpha$ and delays between pulses Δ and $\Delta' = 2\Delta + t_w$. The total duration of either cycle is $t_c = 24\tau$, and $2\tau = \Delta + t_w$.

During the preparation stage, one can view multiple quantum coherence as elements of the density matrix

$$\rho(t) = \exp(-i\overline{H}_D^0 t)\rho(0)\exp(i\overline{H}_D^0 t). \tag{4}$$

In the development of off-diagonal elements of ρ each coupled pair may be described using a set of stationary states $|j\rangle\langle k|$. In the $|j\rangle\langle k|$ notation $\rho(t)$ may be written as

$$\rho(t) = \sum \langle j|\rho(0)|k\rangle \exp[-i(\omega_j - \omega_k)t]|j\rangle\langle k| \tag{5}$$

where ω_j is the eigenfrequency that characterizes eigenstates of the dipolar Hamiltonian. Writing the density operator as a power series expansion gives

$$\rho(t) = \rho(0) + it[\rho(0), \overline{H}_D^0] - \frac{t^2}{2!}[[\rho(0), \overline{H}_D^0], \overline{H}_D^0] + \cdots. \tag{6}$$

The second and higher order terms of the above expansion become significant as the system evolves forward in time under $\overline{H}_D^0$; the nested commutators create product terms which reflect the number N of interacting spins and depend on the magnitude of ω_D and the evolution time. Following the mixing period, the magnetization observed at the point of detection carries all information about the spin system which is governed by the propagators $U = \exp(-i\overline{H}_D^0 t_p)$ and $V = \exp(-i\overline{H}_{D,m}^0 t_m) = \exp(i\overline{H}_D^0 t_m)$ during the preparation (p) and mixing (m) periods, respectively. The detected signal may be written as

$$S(t) = \mathrm{Tr}\{I_z\rho(t)\} = \mathrm{Tr}\{I_z V^+ \exp(-iH_D t)U^+\rho(0)U\exp(iH_D t)V\}, \tag{7}$$

where H_D represents the homonuclear dipolar Hamiltonian defined in Section 2. By experimentally imposing a phase modulation φ on all of the applied pulses during the preparation period the propagator U may be recast as $U_\varphi \equiv \exp(i\varphi I_z)U\exp(-i\varphi I_z)$ and the operation $\langle j|U^+ I_z U^-|k\rangle$ may be written as matrix elements M_{jk}. The signal intensity then becomes a function of the applied phase shift, φ, of

the preparation period with respect to the mixing period. The intensity of any given multiple coherence order, n, may then be measured by performing a Fourier transformation as a function of this phase shift

$$S(t) = \sum |M_{jk}|^2 \exp(in\varphi)\exp[-i(\omega_j - \omega_k)t]. \tag{8}$$

2. Average Hamiltonian theory

In the following we provide a review of the theoretical formalism used to analyze the effects of pulse artifacts in the two multiple pulse sequences considered; the discussion follows closely from [15]. We consider the nuclear spin system in the Larmor rotating frame. In this frame the Hamiltonian has the form

$$H(t) = H_{rf}(t) + H_{int}. \tag{9}$$

In the above expression, $H_{rf}(t)$ is the Hamiltonian from the RF pulse sequence applied to the sample and H_{int} is the internal Hamiltonian which may be written as

$$H_{int} = H_O + H_D \tag{10}$$

where H_O is a resonance offset Hamiltonian or chemical shift Hamiltonian. The homonuclear dipolar interaction, H_D, is given by

$$H_D = -\sum_{j<k} \omega_D(3I_z^j I_z^k - \mathbf{I}^j \cdot \mathbf{I}^k). \tag{11}$$

The equation of motion in the rotating frame is given by the Liouville–von Neumann equation

$$i\frac{d\rho}{dt} = [H, \rho]. \tag{12}$$

To determine the effective Hamiltonian of a series of pulses and periods of free evolution one makes a transformation into the