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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.

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. 1 b–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 Sect. 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 rads/s)

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

where ω_D is the dipolar coupling strength given by

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

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.

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

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

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

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

$$\rho(t) = \sum_j \langle j | \rho(0) | k \rangle \exp[-i(\omega_j - \omega_k)t] |j\rangle \langle k| \quad (5)$$

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

$$\rho(t) = \rho(0) + it \left[\rho(0), \overline{H}_D^0 \right] - \frac{t^2}{2!} \left[\left[\rho(0), \overline{H}_D^0 \right], \overline{H}_D^0 \right] + \dots \quad (6)$$

The second and higher order terms of the above expansion become significant as the system evolves forward in time under $\bar{H}_D^0$; 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 $U = \exp(-i\bar{H}_D^0 t_p)$ and $V = \exp(-i\bar{H}_{D,m}^0 t_m) = \exp(i\bar{H}_D^0 t_m)$ during the preparation (p) and mixing (m) periods, respectively. The detected signal may be written

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

where H_D represents the homonuclear dipolar Hamiltonian defined in Sect. 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 $U_\phi \equiv \exp(i\phi I_z) U \exp(-i\phi I_z)$ 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

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

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

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

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

$$H_{\text{int}} = H_O + H_D \quad (10)$$

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

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

The equation of motion in the rotating frame is given by the Liouvilleon Neumann equation

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

To determine the effective Hamiltonian of a series of pulses and periods of free evolution one makes a transformation into the so-called “toggling frame” where the Hamiltonian’s time dependence may be manipulated via the time dependence of the applied pulses

$$\tilde{\rho}(t) = U_{\text{rf}}^{-1} \rho(t) U_{\text{rf}}. \quad (13)$$

The propagator for $\tilde{\rho}$ is given by

$$i \frac{d\tilde{\rho}}{dt} = [\tilde{H}_{\text{int}}, \tilde{\rho}] \quad (14)$$

with

$$\tilde{H}_{\text{int}}(t) = U_{\text{rf}}(t)^{-1} H_{\text{int}} U_{\text{rf}}(t). \quad (15)$$

In the above expression, H_{int} is time independent in a frame rotating at the Larmor frequency. However, in the new “toggling frame” $\tilde{H}_{\text{int}}(t)$ is time dependent. The propagator which governs the time evolution of the density matrix ρ is written

$$U(t) = U_{\text{rf}}(t) U_{\text{int}}(t). \quad (16)$$

The operator U_{rf} obeys Liouville’s equation of motion

$$i \frac{dU_{\text{rf}}}{dt} = -H_{\text{rf}} U_{\text{rf}}. \quad (17)$$

In terms of the Dyson series the solution of Eq. 17 is given by

$$U_{\text{rf}} = T \exp[-i \int_0^t dt' H_{\text{rf}}(t')] \quad (18)$$

where T is the Dyson time ordering operator. In multiple pulse experiments the RF pulse sequence is often cyclic and the propagator for the RF pulses satisfies $U_{\text{rf}} = \dots U_3 U_2 U_1 = 1$ over a time period termed the cycle time, t_c . The description of the density matrix may be further simplified by introducing a second frame transformation

$$\tilde{\tilde{\rho}} = U_{\text{int}}^{-1} \tilde{\rho}(t) U_{\text{int}}. \quad (19)$$

The propagator $U_{\text{int}}(t_c)$ may be written using the Magnus expansion

$$U_{\text{int}}(t_c) = \exp \{-it_c(\overline{H}_{\text{int}}^0 + \overline{H}_{\text{int}}^1 + \dots)\} \quad (20)$$

where

$$\overline{H}_{\text{int}}^0 = \frac{1}{t_c} \int_0^{t_c} \tilde{H}_{\text{int}}(t) dt \quad (21)$$

$$\bar{H}_{\text{int}}^{-1} = -\frac{i}{2t_c} \int_0^{t_c} dt_2 \int_0^{t_2} dt_1 [\tilde{H}_{\text{int}}(t_2), \tilde{H}_{\text{int}}(t_1)]. \quad (22)$$

The density matrix $\rho(t_c)$ after a cycle of duration t_c is then given by

$$\rho(t_c) = U_{\text{rf}} U_{\text{int}} \rho(0) U_{\text{int}}^{-1} U_{\text{rf}}^{-1}. \quad (23)$$

2.1. Accounting for imperfections

In all multiple pulse NMR experiments the applied RF pulses are not perfect delta functions, may not be completely uniform across the ensemble, and may not have perfectly calibrated or constant phases. Since the sample is exposed to a pulse train many times, even small imperfections can accumulate into large errors. Previous work has considered pulse errors in related spin counting sequences, including a different, earlier double quantum sequence where resonance offsets, chemical shifts, and RF inhomogeneities were examined [16]. The effects of resonance offsets and RF inhomogeneity for the two sequences investigated here have also been mentioned briefly [2]. In this work we quantify and compare the two spin counting sequences' robustness to pulse errors.

Pulse width errors arise simply from pulse calibration errors; the pulse width, t_w , changes the total rotation angle from θ to $\theta(1 + \delta/t_w)$, producing a fractional error δ/t_w . The second error considered is due to RF inhomogeneity. For this error, if θ_j represents the rotation angle acting on the j^{th} nucleus, then one may represent the error due to the inhomogeneity of the RF magnetic field as ϵ_j/t_w ; the total rotation acting on the j^{th} nucleus is thus $\theta_j = \theta(1 + \epsilon_j/t_w)$. The error ϵ_j for an x or $\bar{x}$ pulse associated with the RF field inhomogeneity is expected to be equal, by symmetry. The third error we consider, a phase error, is caused by differences in phase between the x and y components of the pulses in the rotating frame. In the rotating frame the x and y components of an x pulse will be modified to $I_x \cos \phi_x$ and $I_y \sin \phi_x$ respectively so that for small errors ϕ_x (modeled here) the error reduces to $I_y \phi_x$. The fourth error considered, the pulse-transient error, is associated with the fact that tuned RF circuits used in NMR cannot respond to the applied voltage instantaneously. The Hamiltonian associated with this error for a pulse applied along the x axis is written $H_T = \omega_T(t)I_y$, where $\omega_T(t)$ is the difference between an ideal square wave pulse and the actual pulse, which will be discussed in further detail in Sect. 3.1. This model, which is sometimes used in the analysis of multiple pulse NMR sequences [17], accounts for the orthogonal component of a pulse transient only, since the relative effect of a transient on the in-phase component is much smaller than that on the quadrature component.

For these errors, which violate periodicity conditions, one may divide the RF Hamiltonian $H_{\text{rf}}(t)$ as follows

$$H_{\text{rf}}(t) = H_{\text{rf}}^i(t) + H_{\text{rf}}^n(t) \quad (24)$$

where $H_{\text{rf}}^i(t)$ represents the ideal pulse and $H_{\text{rf}}^n(t)$ represents the nonideal parts of the RF pulses. Combining $H_{\text{rf}}^n(t)$ with $H_{\text{int}}(t)$, one may redefine H_{int} as

$$H_{\text{int}} = H_o + H_D + H_{\text{rf}}^n(t) \quad (25)$$

where the noncyclic portion of $H_{\text{rf}}(t)$ is given by a sum of all of the pulse imperfections in Table 1

$$H_{\text{rf}}^n(t) = \sum_k H_k(t). \quad (26)$$

3. Results and Discussion

3.1. Analytical Calculations

Multiple quantum correlations are created by applying multiple iterations of either pulse sequence shown in Fig. 1b or 1c (hereafter referred to as sequences A and B respectively). Either preparation sequence may be represented by a propagator which is composed of m cycles of eight $\pi/2$ pulses, each of duration t_w and delays Δ and Δ' as shown. To simplify the calculations presented we define the pulse duration as $t_w = 2\alpha$ and the cycle time $t_c = 24\tau$. We account for the finite width of the pulses by expressing the delays as $\Delta = 2\tau - 2\alpha$ and $\Delta' = 4\tau - 2\alpha$. In the tables, we introduce the variables

$\Theta_1 = \frac{\pi}{4\alpha}(\alpha - \tau + t)$, $\Theta_2 = \frac{\pi}{4\alpha}(\alpha - 5\tau + t)$, $\Theta_3 = \frac{\pi}{4\alpha}(\alpha - 7\tau + t)$, $\Theta_4 = \frac{\pi}{4\alpha}(\alpha - 11\tau + t)$, $\Theta_5 = \frac{\pi}{4\alpha}(\alpha - 13\tau + t)$, $\Theta_6 = \frac{\pi}{4\alpha}(\alpha - 17\tau + t)$, $\Theta_7 = \frac{\pi}{4\alpha}(\alpha - 19\tau + t)$ and $\Theta_8 = \frac{\pi}{4\alpha}(\alpha - 23\tau + t)$.

The dipole-dipole Hamiltonians in the toggling frame for sequences A and B are given in Tables 2 and 3 respectively. Using Eq. 21 one finds that the zeroth order average dipolar Hamiltonian of either sequence A or B is the double quantum Hamiltonian shown in Eq. 1.

Using Eq. 22 one finds that the first order average Hamiltonian, $\overline{H}_D^1$, is zero for both sequences, and thus the cycles are insensitive to finite pulse width effects to first order. Evolution under this effective Hamiltonian generates even order multiple quantum coherences, while pulse imperfections may create unwanted odd order coherences and/or changes in the intensity of the even order coherences.

The toggling frame Hamiltonians for the offset operator I_z for the two sequences are shown in Table 4. To zeroth and first order of the Magnus expansion both phase encoding schemes yield $\overline{H}_O^0 = 0$ and $\overline{H}_O^1 = 0$ and are expected to behave robustly against small resonance offsets, chemical shifts, or static field inhomogeneity. Tables 5 and 6 show the toggling frame error Hamiltonians for sequences A and B respectively. To zeroth order of the Magnus expansion, $\overline{H}_\varepsilon^0$, $\overline{H}_p^0$, and $\overline{H}_t^0$ are also zero for both sequences. On the other hand, if $\delta_x = \delta_{\overline{x}}$, $\overline{H}_\delta^0 = 0$. If this zeroth order flip error term is zero, then differences between the two cycles arise from first order, first order-cross terms, and higher order terms of the Magnus expansion.

To first order of the Magnus expansion, $\overline{H}_\delta^1$, $\overline{H}_\varepsilon^1$ and $\overline{H}_t^1$ are zero for both pulse sequences, as seen in Table 7. However, $\overline{H}_p^1$ is not zero, but it is the same for both of the pulse sequences. This leaves the first order error-dipolar and error-offset cross terms as the leading contributors for these other errors. When calculating the error-dipolar and error-offset cross terms, the dipolar or offset interaction is only computed between the pulses and is assumed to be zero during the pulses. This approximation is valid in the limit $t_w \ll t_c$, as is normally realized in these experiments.

Focusing on the error-dipolar cross terms we find that both $\overline{H}_{\delta D}^1$ and $\overline{H}_{\varepsilon D}^1$ are zero for sequence B but nonzero for sequence A. This indicates that sequence B should be more robust against pulse flip or RF inhomogeneity errors. The phase-dipolar cross term $\overline{H}_{PD}^1$, is different for A and B; in sequence A it is proportional to $\phi_x + \phi_{\overline{x}}$ while for sequence B it is

proportional to $(\phi_x + \phi_{\bar{x}}) + 2(\phi_x - \phi_{\bar{x}})$. Table 7 shows that the only difference between the two sequences regarding the phase transient-dipolar cross terms is that sequence B is sensitive to antisymmetric phase transients J_1 as well as symmetric phase transients J_2 . In contrast, sequence A is only affected by symmetric phase transients J_2 . These quantities are given by

$$J_1 = \int_0^{t_w} \omega_T(t) (\sin \omega_1 t - \cos \omega_1 t) dt, \quad (27)$$

$$J_2 = \int_0^{t_w} \omega_T(t) (\sin \omega_1 t + \cos \omega_1 t) dt. \quad (28)$$

In the case where $\omega_1 t_w = \pi/2$, J_1 is zero for symmetric phase transients and J_2 is zero for antisymmetric phase transients. In the case of linear response, symmetric transients are not present and the term J_2 is zero.

Referring again to Table 7, the offset-error cross terms are also different between the two sequences for some errors. Specifically, we find that the offset-phase transient term and offset-phase error terms are zero for both sequences. The offset-RF field inhomogeneity terms have the same magnitude but opposite signs for the two sequences but the offset-pulse flip errors are not the same for both sequences. Lastly we find that the offset-dipolar cross terms are also different between the two cycles; $\bar{H}_{do}^1 = 0$ for sequence A, but it is not zero for sequence B. Thus, in the idealized limit of no experimental artifacts but a nonzero offset interaction, $\bar{H}_{do}^1$ may dominate (due to chemical shift anisotropy or other offset interaction) as a leading order correction to $\bar{H}_d^0$ and sequence A would outperform sequence B. In order to avoid any deviation from $\bar{H}_d^0$ due to any terms in the Magnus expansion coming from offset interactions, systems with intrinsic chemical shift anisotropy are not ideal for these studies. Therefore, the next leading order terms in the Magnus expansion involve pulse artifacts and not offset interactions. In the following sections we discuss experimental and simulation studies showing the impact of pulse artifacts on these two sequences.

Next we discuss the symmetry properties of the two cycles. For symmetric pulse cycles $\tilde{H}_{int}(t) = \tilde{H}_{int}(t_c - t)$ and correction terms $\tilde{H}^k$, where k is odd, vanish. For antisymmetric cycles $\tilde{H}_{int}(t) = -\tilde{H}_{int}(t_c - t)$, $\tilde{H}^0 = 0$ and $\tilde{H}^k = 0$ for all k [18, 19, 20]. A summary of the symmetry properties for sequences A and B is given in Table 1. Pulse sequence B is symmetric in pulse flip errors $\tilde{H}_\delta$ but sequence A is antisymmetric in $\tilde{H}_\delta$ only if $\delta_x = \delta_{\bar{x}}$. As shown in Table 5 sequence A satisfies the antisymmetry condition for $\tilde{H}_e$ (corresponding to RF inhomogeneity), and therefore $\bar{H}_e^0$ is zero together with all higher order correction terms. For sequence B, as shown in Table 6, $\tilde{H}_e$ satisfies the symmetry condition which predicts that all odd order terms are zero in the Magnus expansion for this error. These symmetry properties predict, therefore, that for RF inhomogeneities and pulse flip errors, sequence A would outperform sequence B (only if $\delta_x = \delta_{\bar{x}}$). However, because the zeroth and first order terms in the Magnus expansion for these errors are zero in this case, the error-dipolar cross terms may dominate. These cross terms are nonzero for pulse width errors ($\bar{H}_{sd}^1$) and RF inhomogeneities ($\bar{H}_{ed}^1$) for sequence A, whereas they are zero for sequence B.

To summarize, sequence B is expected to outperform sequence A in the presence of RF inhomogeneity and/or pulse width errors where the dipolar-error cross terms are the leading order corrections to $\bar{H}_d^0$. The presence of a phase error and/or phase transient is rather

complex as these terms depend on both the sum of J_1 and J_2 and the difference in phase $3\phi_x - \phi_x$ for sequence B and J_2 and $\phi_x + \phi_x$ for sequence A. In situations where an offset interaction is present, the offset-dipolar cross term for sequence B is nonzero and there are differences in the RF inhomogeneity-offset and pulse flip error-offset cross terms between sequence A and sequence B.

3.2. Experimental

Experiments were performed at 25°C using a sample of adamantane on a Tecmag Apollo NMR spectrometer at 179.44 MHz. The RF coil in our probe had a quality factor Q of approximately 200, and was tuned to the Larmor precession frequency. Adamantane is a plastic crystal in which intramolecular dipolar interactions are averaged to zero and the spins only interact through intermolecular dipolar interactions with all other spins in the sample. This system has been frequently used for time reversal [12] and decoherence [11] experiments. Six loops of either of the eight-pulse sequences described above were used, with a preparation time $t_c = 74.4 \mu\text{s}$. For the mixing period, a pulse sequence was used with the same pulse width and delays, but with RF phases y and $\bar{y}$, yielding the mixing period average Hamiltonian given in Eq. 3. During the mixing period the multiple-quantum coherences are converted into observable coherences, and a final $\pi/2$ pulse is applied to rotate magnetization to the transverse plane so that the signal may be observed. The nominal preparation and mixing period parameters used in both sequences were $t_w = 4 \mu\text{s}$ ($\omega_1 = 0.393 \times 10^6 \text{ rad/s}$), $\Delta' = 8.4 \mu\text{s}$, and $\Delta = 2.2 \mu\text{s}$.

Figure 2 shows spectra where only even order coherences are observed and these data are taken as the reference spectra to be compared to those where errors are intentionally introduced (below). The spectrum acquired with sequence B appears to offer a higher signal intensity $I(n)$ than that from sequence A; the difference may be due to a combination of effects including residual pulse width errors and RF inhomogeneity artifacts. We quantified the degree of RF inhomogeneity by measuring the signal intensities after a 450 and 90 degree pulse; on the probe used in these studies we found $I_{450}/I_{90} = 0.68$.

Figure 3 a–f shows experimental data where the pulse flip error was systematically varied. The pulse width was varied from $4.2 \mu\text{s}$ to $5.0 \mu\text{s}$ resulting in a rotation of 94.5° to 113° (the left column refers to sequence A and the right column corresponds to sequence B). For each pulse width error, the delays Δ and Δ' were recalculated in order to retain a cycle time of $t_c = 74.4 \mu\text{s}$. In the analytical calculations the zeroth order pulse width error Hamiltonian is proportional to the difference $\delta_{\bar{x}} - \delta_x$ and may be zero if this difference is zero. In (c) and (d) the spectra show that a flip error of 15 percent (corresponding to a pulse width of $4.6 \mu\text{s}$) results in a significant degradation of signal intensity for both pulse sequences. However,

sequence B has a first order pulse flip error-dipolar cross term ($\bar{H}_{\delta d}^1$) equal to zero while it is nonzero for sequence A. In addition, sequence B possesses symmetry properties for $\bar{H}_{\delta}$ while sequence A is only antisymmetric if pulse width errors are the same (i.e. $\delta_{\bar{x}} = \delta_x$). Figure 3 a–b confirms that with a pulse error of approximately 5 percent, sequence B performs better than sequence A, as observed by a smaller reduction in signal intensity (e.g. 6% vs. 32% for the second order coherences).

To provide further information and for comparison with common analysis methods of these datasets [2] we have measured the number of coupled spins, N , by fitting the distribution of measured quantum coherences to a Gaussian and tabulate the results for both cycles in Table 8. Pulse flip errors affect the measurement of N in sequence A more strongly than sequence B. By using a $4.2 \mu\text{s}/94.5^\circ$ pulse, $N=71 \pm 8$ for sequence A and 110 ± 9 for sequence B (the baseline case, as shown in Table 8, gave 106 ± 9 for sequence A and 113 ± 9 for sequence B). We have also quantified differences in the performance of these two sequences in the

presence of pulse flip errors by measuring the ratio of the second to zeroth, first to second, fourth to second, and tenth to second order quantum coherence as given in Table 9. It should be pointed out that for each sequence the baseline data (using a $4.0 \mu\text{s}/90^\circ$ pulse) in each column has been normalized to unity for purposes of comparison. Referring to Table 9, we find that pulse errors introduce a relatively larger single quantum coherence signal in sequence A than in sequence B. Furthermore, Table 9 shows that the ratio of zeroth to second, fourth to second, and tenth to second order quantum coherences are better preserved in sequence B than in sequence A as the pulse flip error is introduced, consistent with the calculations of N in Table 8 and the average Hamiltonian treatment.

3.3. Simulations

While pulse artifacts such as phase transients and phase errors on NMR spectrometers are usually straightforward to measure using well known methods [17], [21] their contribution to the degradation of the two spin counting cycles may be investigated in a more controlled fashion using quantum simulations. One specific challenge for the sequences considered here is that the first order dipolar-phase error cross term in sequence A is proportional to $\phi_x + \phi_{\bar{x}}$ whereas for sequence B it scales as $3\phi_x - \phi_{\bar{x}}$. To our knowledge, there is no systematic method to experimentally measure these two quantities, but only the phase difference $\phi_x - \phi_{\bar{x}}$.

Simulations were performed using 8-spin 1D quantum spin-1/2 chains (though we also confirmed findings on 6- and 10-spin systems). The chains are oriented as rings along a plane transverse to the applied magnetic field, and the simulations are performed in the Larmor rotating reference frame. A similar geometry has been used in studies of the short time multiple quantum dynamics of dipolar coupled spins [22, 23]. Initially only one of the spins is polarized and the dipolar coupling between all pairs of spins is included, i.e. they are coupled by the secular dipolar Hamiltonian given by Eq. 11. The distance between spins r_{nom} was modulated by executing 11 different simulations with the separation between adjacent spins changed by up to $\pm 10\%$ and averaging the results for all spin spacings. The density matrix for the system is evolved under RF and dipolar Hamiltonians using parameters $\mu_0\hbar\gamma^2/(8\pi r_{\text{nom}}^2)=40000 \text{ rad/s}$ and $t_w = 5 \times 10^{-7} \text{ s}$. The evolution time between the preparation and mixing periods was $2 \times 10^{-6} \text{ s}$, and $\Delta = 2.2 \times 10^{-6} \text{ s}$. In the simulation of phase transients shown in Fig. 6, both symmetric and antisymmetric models were studied. Specifically, the model used an ideal x pulse and y components parameterized by

$$\omega_T(t) = \begin{cases} S, & t < t_w/3 \\ 0, & t_w/3 < t < 2t_w/3 \\ \pm S, & 2t_w/3 < t < t_w \end{cases} \quad (29)$$

for symmetric/antisymmetric pulses, where S is varied from 0 to 1/6 the amplitude of the x component of the pulse. Symmetric and antisymmetric phase transients in NMR spectrometers have been discussed in detail elsewhere (see e.g. page 184 of [18] as well as [24]).

Figure 4 shows simulated second order spin correlations under the presence of flip errors for 8 spin, 2 loop simulations with sequences A and B. The signal for sequence B stays closer to its error-free value better than for sequence A (going up to 700% of the error-free value vs. 1100% of the error free value for 2.38° flip errors). This result is in agreement with the average Hamiltonian predictions from Table 7 and the experimental data shown in Fig. 3

since $\overline{H}_{\text{dd}}^1$ is zero for sequence B but is nonzero for sequence A. In Fig. 5 we show the results for 8 spin, 10 loop simulations in the presence of an RF inhomogeneity. Specifically,

different flip error simulations were combined with errors ranging from 0 degrees in the center of the sample to 1.5° at the edges, and then weighted with a cosine function where the edges were weighted less ($\approx 20\%$ less) than the center. These simulations are also consistent with the average Hamiltonian calculations since the leading order correction $\bar{H}_{ed}^1$ is zero for sequence B, but not for sequence A, as seen in Table 7. As seen in the figures, the multiple quantum signal intensity degrades more ($\approx 9\%$ for the second order coherences) using sequence A than sequence B ($\approx 5\%$ for the second order coherences).

In Fig. 6 the results of 8 spin, 2 loop simulations are shown for sequences A and B in the presence of symmetric and antisymmetric phase transients. For symmetric transients, sequences A and B perform similarly with increasing phase transient amplitude (differing by much less than 1% from each other over the range of transient amplitudes simulated). However, for antisymmetric transients, sequence B is more strongly affected than A, having decreased by 15% over the range of transients simulated versus 7% for sequence A. This is consistent with the average Hamiltonian calculations as seen in Table 7 where sequence B is affected by both symmetric (J_2) and antisymmetric (J_1) phase transient components while sequence A is only affected by symmetric transients to first order in the Magnus expansion.

In Fig. 7 the double quantum signal intensity is shown in the presence of phase errors between x and y for an 8 spin quantum simulation using two loops of either pulse sequence A or B. The main result from these simulations is that an error on an x pulse in sequence B causes the largest deviation (53% vs. $\sim 10\%$ for the other phase errors) from the ideal case, in agreement with the average Hamiltonian calculations in Table 7. Specifically, an x phase error in sequence B has a first order term in the Magnus expansion three times larger in magnitude than errors in sequence A or an $\bar{x}$ phase error in sequence B. Lastly, errors on $\bar{x}$ for sequence A or B, and errors on x pulses for sequence A, show similar degradations with increasing phase error (between 9–14%), consistent with the terms $\bar{H}_{pd}^1$ in Table 7.

4. Conclusions

In this work we have investigated the effects of pulse artifacts and offset interactions on two well-known spin counting sequences. We have found that both pulse sequences result in the suppression of I_z Hamiltonians to both zeroth and first order. For pulse flip errors, phase errors, RF inhomogeneity, and phase transients we find that sequences A and B have different sensitivities. Sequence B outperforms sequence A in the presence of RF inhomogeneities and pulse flip errors. For phase errors on x pulses and for antisymmetric phase transient errors, pulse sequence A outperforms pulse sequence B. Simulations and experiments reveal signal intensity changes under the influence of these errors and corroborate the analytical calculations. It is expected that these distortions can be mitigated by accurate tuning of the probe using well-known methods [21], or by second averaging schemes [25]. Finally, because these pulse sequences are not limited by finite pulse width effects to first order, their use for time-reversal experiments [12] may be preferred over magic echo cycles, which suffer degradation in efficiency because of finite pulse widths, especially for long echo times [26, 27].

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Figure 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 $2\tau = \Delta + t_w$.

Figure 2.

Proton multiple quantum spectra for experiments on adamantane obtained under baseline conditions for (a) pulse sequence A and (b) sequence B. The cycle time for these experiments and for all others reported here was held fixed at $\tau_c = 74.4 \mu\text{s}$. The number of repeated cycles is $m = 6$, and the width of the $\pi/2$ pulses is $2a = t_w = 4.0 \mu\text{s}$. During the excitation time, multiple-spin correlations are created and the distribution of the signal intensity $I(n)$ over the coherence order n is plotted in this graph.

Figure 3.

Dependence of the multiple quantum spectra of adamantane on an artificially introduced experimental pulse error, for t_w equal to (a) and (b) 4.2, (c) and (d) 4.6, (e) and (f) 5.0 in μs for two pulse sequences (the baseline pulse width $t_w = 4.0 \mu\text{s}$). Figures (a), (c), and (e) correspond to sequence A and (b), (d), and (f) to sequence B, shown in Figure 1.

Figure 4.

Variation of the double quantum intensity versus flip angle error for sequences A and B in 8 spin quantum simulations. The observed variation in the second order coherence as a function of the pulse flip error is larger for sequence A than for sequence B, due to the differences in $\overline{H}_{\delta D}^{-1}$ in Table 7. In this figure, $\blacktriangle$ represents sequence A and $\blacksquare$ represents sequence B.

Figure 5.

Multiple quantum spectra for 8 spin, 10 loop simulations for sequence A (a) and B (b). The black lines show results where there is no introduced RF inhomogeneity, while the red lines show results with a 1.5° difference in flip angle across the sample, as described in the text. The degradation in the multiple quantum signal intensities ($\approx 9\%$ for second order) is greater for sequence A than for sequence B ($\approx 5\%$ for second order), in agreement with average Hamiltonian calculations for $\overline{H}_{eD}^{-1}$ shown in Table 7.

Figure 6.

Double quantum signal intensity in the presence of RF phase transients for 8 spin quantum simulations using two loops of either pulse sequence A or B. In this figure, ▲ represents sequence A with symmetric phase transients, ▼ represents sequence A with antisymmetric phase transients, ■ represents sequence B with symmetric phase transients, and ★ represents sequence B with antisymmetric phase transients. The units of the x axis here refer to the amplitude of the transient (y for x pulses) components of the pulses, (in percent) relative to that of the ideal pulse amplitude. In the case of symmetric transients, sequences A and B perform similarly with increasing phase transient amplitude. However, for antisymmetric transients, sequence B is more strongly affected than A, due to the terms $\bar{H}_{TD}^1$ in Table 7.

Figure 7.

Double quantum signal intensity in the presence of phase errors applied to x or $\bar{x}$ pulses for an 8 spin quantum simulation using two loops of either sequence A or B. In this figure, ▲ represents sequence A with phase errors on x , ▼ represents sequence A with phase errors on $\bar{x}$, ■ represents sequence B with phase errors on x , and ★ represents sequence B with phase errors on $\bar{x}$. This figure shows a larger degradation of the second order intensity in sequence B for phase errors on x pulses, consistent with the values of $\overline{H}_{PD}^1$ given in Table 7. The other three cases, phase errors for sequence A pulses along x or $\bar{x}$ and phase errors for $\bar{x}$ pulses, give similar degradation in signal intensity, also consistent with average Hamiltonian calculations.

Table 1

Hamiltonians corresponding to nonidealities in a radio-frequency pulse along the x axis. Sequence A and B refer to the sequences in Figs. 1b and 1c respectively. For each error the symmetry properties of either cycle are tabulated and described further in the text. A symmetric toggling frame Hamiltonian will cause odd order terms in the Magnus expansion to vanish, while antisymmetric toggling frame Hamiltonians cause all terms in the Magnus expansion to vanish.

Radio-frequency imperfection (for x pulses)	Hamiltonian	Symmetry (Sequence A)	Symmetry (Sequence B)
Pulse-width error	$H_{\delta} = \frac{\delta_x}{t_w} I_x$	N/A	Symmetric
RF field inhomogeneity for the i^{th} nucleus	$H_{\varepsilon} = -\frac{\varepsilon_i}{t_w} I_{xi}$	Antisymmetric	Symmetric
Phase error by angle ϕ (small errors)	$H_P \cong -\omega_1 I_y \phi_x$	N/A	N/A
Pulse-transient phase error	$H_T = \omega T(t) I_y$	N/A	N/A

Table 2

Transformations of dipole-dipole Hamiltonians with finite pulse widths for the sequence shown in Fig. 1b. The angles Θ_n ($n = 1, \dots, 8$) are defined in the text.

Interval	Time	Toggleing Frame Hamiltonian $\widetilde{H}_D$
δ_1	$0 \leq t < \tau - a$	$-\omega_D [3I_z^1 I_z^2 - I^1 \cdot I^2]$
δ_2	$\tau - a \leq t < \tau + a$	$-\omega_D [3(I_z^1 \cos \Theta_1 - I_y^1 \sin \Theta_1)(I_z^2 \cos \Theta_1 - I_y^2 \sin \Theta_1) - I^1 \cdot I^2]$
δ_3	$\tau + a < t < 5\tau - a$	$-\omega_D [3I_y^1 I_y^2 - I^1 \cdot I^2]$
δ_4	$5\tau - a \leq t < 5\tau + a$	$-\omega_D [3(-I_y^1 \cos \Theta_2 - I_z^1 \sin \Theta_2)(-I_y^2 \cos \Theta_2 - I_z^2 \sin \Theta_2) - I^1 \cdot I^2]$
δ_5	$5\tau + a < t < 7\tau - a$	$-\omega_D [3I_z^1 I_z^2 - I^1 \cdot I^2]$
δ_6	$7\tau - a \leq t < 7\tau + a$	$-\omega_D [3(-I_z^1 \cos \Theta_3 + I_y^1 \sin \Theta_3)(-I_z^2 \cos \Theta_3 + I_y^2 \sin \Theta_3) - I^1 \cdot I^2]$
δ_7	$7\tau + a < t < 11\tau - a$	$-\omega_D [3I_y^1 I_y^2 - I^1 \cdot I^2]$
δ_8	$11\tau - a \leq t < 11\tau + a$	$-\omega_D [3(I_y^1 \cos \Theta_4 + I_z^1 \sin \Theta_4)(I_y^2 \cos \Theta_4 + I_z^2 \sin \Theta_4) - I^1 \cdot I^2]$
δ_9	$11\tau + a < t < 13\tau - a$	$-\omega_D [3I_z^1 I_z^2 - I^1 \cdot I^2]$
δ_{10}	$13\tau - a \leq t < 13\tau + a$	$-\omega_D [3(I_z^1 \cos \Theta_5 + I_y^1 \sin \Theta_5)(I_z^2 \cos \Theta_5 + I_y^2 \sin \Theta_5) - I^1 \cdot I^2]$
δ_{11}	$13\tau + a < t < 17\tau - a$	$-\omega_D [3I_y^1 I_y^2 - I^1 \cdot I^2]$
δ_{12}	$17\tau - a \leq t < 17\tau + a$	$-\omega_D [3(I_y^1 \cos \Theta_6 - I_z^1 \sin \Theta_6)(I_y^2 \cos \Theta_6 - I_z^2 \sin \Theta_6) - I^1 \cdot I^2]$
δ_{13}	$17\tau + a < t < 19\tau - a$	$-\omega_D [3I_z^1 I_z^2 - I^1 \cdot I^2]$
δ_{14}	$19\tau - a \leq t < 19\tau + a$	$-\omega_D [3(-I_z^1 \cos \Theta_7 - I_y^1 \sin \Theta_7)(-I_z^2 \cos \Theta_7 - I_y^2 \sin \Theta_7) - I^1 \cdot I^2]$
δ_{15}	$19\tau + a < t < 23\tau - a$	$-\omega_D [3I_y^1 I_y^2 - I^1 \cdot I^2]$
δ_{16}	$23\tau - a \leq t < 23\tau + a$	$-\omega_D [3(-I_y^1 \cos \Theta_8 + I_z^1 \sin \Theta_8)(-I_y^2 \cos \Theta_8 + I_z^2 \sin \Theta_8) - I^1 \cdot I^2]$
δ_{17}	$23\tau + a < t < 24\tau$	$-\omega_D [3I_z^1 I_z^2 - I^1 \cdot I^2]$

Table 3

Transformations of dipole-dipole Hamiltonians with finite pulse widths for the sequence shown in Fig. 1c. The angles Θ_n ($n = 1, \dots, 8$) are defined in the text.

Interval	Time	Toggleing Frame Hamiltonian $\widetilde{H}_D$
δ_1	$0 \leq t < \tau - a$	$-\omega_D [3I_z^1 I_z^2 - I^1 \cdot I^2]$
δ_2	$\tau - a \leq t < \tau + a$	$-\omega_D [3(I_z^1 \cos \Theta_1 - I_y^1 \sin \Theta_1)(I_z^2 \cos \Theta_1 - I_y^2 \sin \Theta_1) - I^1 \cdot I^2]$
δ_3	$\tau + a < t < 5\tau - a$	$-\omega_D [3I_y^1 I_y^2 - I^1 \cdot I^2]$
δ_4	$5\tau - a \leq t < 5\tau + a$	$-\omega_D [3(-I_y^1 \cos \Theta_2 - I_z^1 \sin \Theta_2)(-I_y^2 \cos \Theta_2 - I_z^2 \sin \Theta_2) - I^1 \cdot I^2]$
δ_5	$5\tau + a < t < 7\tau - a$	$-\omega_D [3I_z^1 I_z^2 - I^1 \cdot I^2]$
δ_6	$7\tau - a \leq t < 7\tau + a$	$-\omega_D [3(-I_z^1 \cos \Theta_3 - I_y^1 \sin \Theta_3)(-I_z^2 \cos \Theta_3 - I_y^2 \sin \Theta_3) - I^1 \cdot I^2]$
δ_7	$7\tau + a < t < 11\tau - a$	$-\omega_D [3I_y^1 I_y^2 - I^1 \cdot I^2]$
δ_8	$11\tau - a \leq t < 11\tau + a$	$-\omega_D [3(-I_y^1 \cos \Theta_4 + I_z^1 \sin \Theta_4)(-I_y^2 \cos \Theta_4 + I_z^2 \sin \Theta_4) - I^1 \cdot I^2]$
δ_9	$11\tau + a < t < 13\tau - a$	$-\omega_D [3I_z^1 I_z^2 - I^1 \cdot I^2]$
δ_{10}	$13\tau - a \leq t < 13\tau + a$	$-\omega_D [3(I_z^1 \cos \Theta_5 + I_y^1 \sin \Theta_5)(I_z^2 \cos \Theta_5 + I_y^2 \sin \Theta_5) - I^1 \cdot I^2]$
δ_{11}	$13\tau + a < t < 17\tau - a$	$-\omega_D [3I_y^1 I_y^2 - I^1 \cdot I^2]$
δ_{12}	$17\tau - a \leq t < 17\tau + a$	$-\omega_D [3(I_y^1 \cos \Theta_6 - I_z^1 \sin \Theta_6)(I_y^2 \cos \Theta_6 - I_z^2 \sin \Theta_6) - I^1 \cdot I^2]$
δ_{13}	$17\tau + a < t < 19\tau - a$	$-\omega_D [3I_z^1 I_z^2 - I^1 \cdot I^2]$
δ_{14}	$19\tau - a \leq t < 19\tau + a$	$-\omega_D [3(-I_z^1 \cos \Theta_7 + I_y^1 \sin \Theta_7)(-I_z^2 \cos \Theta_7 + I_y^2 \sin \Theta_7) - I^1 \cdot I^2]$
δ_{15}	$19\tau + a < t < 23\tau - a$	$-\omega_D [3I_y^1 I_y^2 - I^1 \cdot I^2]$
δ_{16}	$23\tau - a \leq t < 23\tau + a$	$-\omega_D [3(I_y^1 \cos \Theta_8 + I_z^1 \sin \Theta_8)(I_y^2 \cos \Theta_8 + I_z^2 \sin \Theta_8) - I^1 \cdot I^2]$
δ_{17}	$23\tau + a < t < 24\tau$	$-\omega_D [3I_z^1 I_z^2 - I^1 \cdot I^2]$

Table 4

Transformations of the operator I_z for the eight-pulse spin counting sequences (assuming finite pulse width effects) shown in Fig. 1. The angles Θ_n ($n = 1, \dots, 8$) are defined in the text.

Interval	Time	$\widetilde{H}_O$ sequence A	$\widetilde{H}_O$ sequence B
δ_1	$0 \leq t < \tau - a$	$\alpha(I_z)$	$\alpha(I_z)$
δ_2	$\tau - a \leq t < \tau + a$	$\alpha(I_z \cos \Theta_1 - I_y \sin \Theta_1)$	$\alpha(I_z \cos \Theta_1 - I_y \sin \Theta_1)$
δ_3	$\tau + a < t < 5\tau - a$	$\alpha(-I_y)$	$\alpha(-I_y)$
δ_4	$5\tau - a \leq t < 5\tau + a$	$\alpha(-I_y \cos \Theta_2 - I_z \sin \Theta_2)$	$\alpha(-I_y \cos \Theta_2 - I_z \sin \Theta_2)$
δ_5	$5\tau + a < t < 7\tau - a$	$\alpha(-I_z)$	$\alpha(-I_z)$
δ_6	$7\tau - a \leq t < 7\tau + a$	$\alpha(-I_z \cos \Theta_3 + I_y \sin \Theta_3)$	$\alpha(-I_z \cos \Theta_3 - I_y \sin \Theta_3)$
δ_7	$7\tau + a < t < 11\tau - a$	$\alpha(I_y)$	$\alpha(-I_y)$
δ_8	$11\tau - a \leq t < 11\tau + a$	$\alpha(I_y \cos \Theta_4 + I_z \sin \Theta_4)$	$\alpha(-I_y \cos \Theta_4 + I_z \sin \Theta_4)$
δ_9	$11\tau + a < t < 13\tau - a$	$\alpha(I_z)$	$\alpha(I_z)$
δ_{10}	$13\tau - a \leq t < 13\tau + a$	$\alpha(I_z \cos \Theta_5 + I_y \sin \Theta_5)$	$\alpha(I_z \cos \Theta_5 + I_y \sin \Theta_5)$
δ_{11}	$13\tau + a < t < 17\tau - a$	$\alpha(I_y)$	$\alpha(I_y)$
δ_{12}	$17\tau - a \leq t < 17\tau + a$	$\alpha(I_y \cos \Theta_6 - I_z \sin \Theta_6)$	$\alpha(I_y \cos \Theta_6 - I_z \sin \Theta_6)$
δ_{13}	$17\tau + a < t < 19\tau - a$	$\alpha(-I_z)$	$\alpha(-I_z)$
δ_{14}	$19\tau - a \leq t < 19\tau + a$	$\alpha(-I_z \cos \Theta_7 - I_y \sin \Theta_7)$	$\alpha(-I_z \cos \Theta_7 + I_y \sin \Theta_7)$
δ_{15}	$19\tau + a < t < 23\tau - a$	$\alpha(-I_y)$	$\alpha(I_y)$
δ_{16}	$23\tau - a \leq t < 23\tau + a$	$\alpha(-I_y \cos \Theta_8 + I_z \sin \Theta_8)$	$\alpha(I_y \cos \Theta_8 + I_z \sin \Theta_8)$
δ_{17}	$23\tau + a < t < 24\tau$	$\alpha(I_z)$	$\alpha(I_z)$

Table 5

Toggling frame Hamiltonians for errors shown in Table 1 for the spin-counting sequence shown in Fig. 1b (sequence A). As discussed in the text, the toggling frame Hamiltonians refer to pulse flip errors ($\widetilde{H}_\delta$), RF inhomogeneity ($\widetilde{H}_\varepsilon$), phase errors ($\widetilde{H}_p$), and phase transients ($\widetilde{H}_t$). The angles Θ_n ($n = 1, \dots, 8$) are also defined in the text.

Int.	Time	$\widetilde{H}_\delta$	$\widetilde{H}_\varepsilon$	$\widetilde{H}_p$	$\widetilde{H}_t$
δ_1	0 $t < \tau - a$	0	0	0	0
δ_2	$\tau - a$ t $\tau + a$	$-\frac{\delta_X}{I_{\text{rf}}} I_X$	$-\frac{\varepsilon_I}{I_{\text{rf}}} I_{\text{rf}}$	$-\omega_1 \phi_A(I_Y \cos \Theta_1 + I_Z \sin \Theta_1)$	$\omega_T(O(I_Y \cos \Theta_1 + I_Z \sin \Theta_1))$
δ_3	$\tau + a < t < 5\tau - a$	0	0	0	0
δ_4	$5\tau - a$ t $5\tau + a$	$-\frac{\delta_X}{I_{\text{rf}}} I_X$	$-\frac{\varepsilon_I}{I_{\text{rf}}} I_{\text{rf}}$	$-\omega_1 \phi_A(I_Z \cos \Theta_2 - I_Y \sin \Theta_2)$	$\omega_T(O(I_Z \cos \Theta_2 - I_Y \sin \Theta_2))$
δ_5	$5\tau + a < t < 7\tau - a$	0	0	0	0
δ_6	$7\tau - a$ t $7\tau + a$	$-\frac{\delta_X}{I_{\text{rf}}} I_X$	$-\frac{\varepsilon_I}{I_{\text{rf}}} I_{\text{rf}}$	$-\omega_1 \phi_A(-I_Y \cos \Theta_3 - I_Z \sin \Theta_3)$	$\omega_T(O(-I_Y \cos \Theta_3 - I_Z \sin \Theta_3))$
δ_7	$7\tau + a < t < 11\tau - a$	0	0	0	0
δ_8	$11\tau - a$ t $11\tau + a$	$-\frac{\delta_X}{I_{\text{rf}}} I_X$	$-\frac{\varepsilon_I}{I_{\text{rf}}} I_{\text{rf}}$	$-\omega_1 \phi_A(-I_Z \cos \Theta_4 + I_Y \sin \Theta_4)$	$\omega_T(O(-I_Z \cos \Theta_4 + I_Y \sin \Theta_4))$
δ_9	$11\tau + a < t < 13\tau - a$	0	0	0	0
δ_{10}	$13\tau - a$ t $13\tau + a$	$\frac{\delta_X}{I_{\text{rf}}} I_X$	$\frac{\varepsilon_I}{I_{\text{rf}}} I_{\text{rf}}$	$\omega_1 \phi_A(I_Y \cos \Theta_5 - I_Z \sin \Theta_5)$	$-\omega_T(O(I_Y \cos \Theta_5 - I_Z \sin \Theta_5))$
δ_{11}	$13\tau + a < t < 17\tau - a$	0	0	0	0
δ_{12}	$17\tau - a$ t $17\tau + a$	$\frac{\delta_X}{I_{\text{rf}}} I_X$	$\frac{\varepsilon_I}{I_{\text{rf}}} I_{\text{rf}}$	$\omega_1 \phi_A(-I_Z \cos \Theta_6 - I_Y \sin \Theta_6)$	$-\omega_T(O(-I_Z \cos \Theta_6 - I_Y \sin \Theta_6))$
δ_{13}	$17\tau + a < t < 19\tau - a$	0	0	0	0
δ_{14}	$19\tau - a$ t $19\tau + a$	$\frac{\delta_X}{I_{\text{rf}}} I_X$	$\frac{\varepsilon_I}{I_{\text{rf}}} I_{\text{rf}}$	$\omega_1 \phi_A(-I_Y \cos \Theta_7 + I_Z \sin \Theta_7)$	$-\omega_T(O(-I_Y \cos \Theta_7 + I_Z \sin \Theta_7))$
δ_{15}	$19\tau + a < t < 23\tau - a$	0	0	0	0
δ_{16}	$23\tau - a$ t $23\tau + a$	$\frac{\delta_X}{I_{\text{rf}}} I_X$	$\frac{\varepsilon_I}{I_{\text{rf}}} I_{\text{rf}}$	$\omega_1 \phi_A(I_Z \cos \Theta_8 + I_Y \sin \Theta_8)$	$-\omega_T(O(I_Z \cos \Theta_8 + I_Y \sin \Theta_8))$
δ_{17}	$23\tau + a < t$ 24τ	0	0	0	0

Table 6

Toggle frame Hamiltonians for errors shown in Table 1 for the spin-counting sequence shown in Fig. 1c (sequence B). As discussed in the text, the toggle frame Hamiltonians refer to pulse flip errors ($\widetilde{H}_\delta$), RF inhomogeneity ($\widetilde{H}_\varepsilon$), phase errors ($\widetilde{H}_p$), and phase transients ($\widetilde{H}_\tau$). The angles Θ_n ($n = 1, \dots, 8$) are also defined in the text.

Int.	Time	$\widetilde{H}_\delta$	$\widetilde{H}_\varepsilon$	$\widetilde{H}_p$	$\widetilde{H}_\tau$
δ_1	0 $t < \tau - a$	0	0	0	0
δ_2	$\tau - a$ t $\tau + a$	$-\frac{\delta_X}{I_{H\nu}} I_X$	$-\frac{\varepsilon_I}{I_{H\nu}} I_{XI}$	$-\omega_1 \phi_X (I_Y \cos \Theta_1 + I_Z \sin \Theta_1)$	$\omega_7 \phi (I_Y \cos \Theta_1 + I_Z \sin \Theta_1)$
δ_3	$\tau + a < t < 5\tau - a$	0	0	0	0
δ_4	5 $\tau - a$ t 5 $\tau + a$	$-\frac{\delta_X}{I_{H\nu}} I_X$	$-\frac{\varepsilon_I}{I_{H\nu}} I_{XI}$	$-\omega_1 \phi_X (I_Z \cos \Theta_2 - I_Y \sin \Theta_2)$	$\omega_7 \phi (I_Z \cos \Theta_2 - I_Y \sin \Theta_2)$
δ_5	5 $\tau + a < t < 7\tau - a$	0	0	0	0
δ_6	7 $\tau - a$ t 7 $\tau + a$	$\frac{\delta_X}{I_{H\nu}} I_X$	$\frac{\varepsilon_I}{I_{H\nu}} I_{XI}$	$\omega_1 \phi_X (-I_Y \cos \Theta_3 + I_Z \sin \Theta_3)$	$-\omega_7 \phi (-I_Y \cos \Theta_3 + I_Z \sin \Theta_3)$
δ_7	7 $\tau + a < t < 11\tau - a$	0	0	0	0
δ_8	11 $\tau - a$ t 11 $\tau + a$	$\frac{\delta_X}{I_{H\nu}} I_X$	$\frac{\varepsilon_I}{I_{H\nu}} I_{XI}$	$\omega_1 \phi_X (I_Z \cos \Theta_4 + I_Y \sin \Theta_4)$	$-\omega_7 \phi (I_Z \cos \Theta_4 + I_Y \sin \Theta_4)$
δ_9	11 $\tau + a < t < 13\tau - a$	0	0	0	0
δ_{10}	13 $\tau - a$ t 13 $\tau + a$	$\frac{\delta_X}{I_{H\nu}} I_X$	$\frac{\varepsilon_I}{I_{H\nu}} I_{XI}$	$\omega_1 \phi_X (I_Y \cos \Theta_5 - I_Z \sin \Theta_5)$	$-\omega_7 \phi (I_Y \cos \Theta_5 - I_Z \sin \Theta_5)$
δ_{11}	13 $\tau + a < t < 17\tau - a$	0	0	0	0
δ_{12}	17 $\tau - a$ t 17 $\tau + a$	$\frac{\delta_X}{I_{H\nu}} I_X$	$\frac{\varepsilon_I}{I_{H\nu}} I_{XI}$	$\omega_1 \phi_X (-I_Z \cos \Theta_6 - I_Y \sin \Theta_6)$	$-\omega_7 \phi (-I_Z \cos \Theta_6 - I_Y \sin \Theta_6)$
δ_{13}	17 $\tau + a < t < 19\tau - a$	0	0	0	0
δ_{14}	19 $\tau - a$ t 19 $\tau + a$	$-\frac{\delta_X}{I_{H\nu}} I_X$	$-\frac{\varepsilon_I}{I_{H\nu}} I_{XI}$	$-\omega_1 \phi_X (-I_Y \cos \Theta_7 - I_Z \sin \Theta_7)$	$\omega_7 \phi (-I_Y \cos \Theta_7 - I_Z \sin \Theta_7)$
δ_{15}	19 $\tau + a < t < 23\tau - a$	0	0	0	0
δ_{16}	23 $\tau - a$ t 23 $\tau + a$	$-\frac{\delta_X}{I_{H\nu}} I_X$	$-\frac{\varepsilon_I}{I_{H\nu}} I_{XI}$	$-\omega_1 \phi_X (-I_Z \cos \Theta_8 + I_Y \sin \Theta_8)$	$\omega_7 \phi (-I_Z \cos \Theta_8 + I_Y \sin \Theta_8)$
δ_{17}	23 $\tau + a < t$ 24 τ	0	0	0	0

Table 7

Leading order terms of the Magnus expansion through first order for the two eight-pulse spin-counting sequences considered in this work. In the table $\bar{H}_o^0$ and $\bar{H}_o^1$ are the zeroth and first order offset average Hamiltonians associated with I_z interactions. $\bar{H}_D^0$ and $\bar{H}_D^1$ are the zeroth and first order dipolar Hamiltonians respectively and $\bar{H}_{DO}^1$ is the first order dipolar-offset cross term. $\bar{H}_\delta^0, \bar{H}_\varepsilon^0, \bar{H}_p^0, \bar{H}_T^0, \bar{H}_\delta^1, \bar{H}_\varepsilon^1, \bar{H}_p^1, \bar{H}_T^1$ are the zeroth and first order average Hamiltonians corresponding to imperfections given in Table 1. $\bar{H}_{PD}^1, \bar{H}_{TD}^1, \bar{H}_{\delta D}^1$, and $\bar{H}_{\varepsilon D}^1$ are the average Hamiltonians for the phase error-, phase transient-, pulse flip error-, and RF inhomogeneity-dipolar cross terms respectively. Similarly, $\bar{H}_{PO}^1, \bar{H}_{TO}^1, \bar{H}_{\delta O}^1$, and $\bar{H}_{\varepsilon O}^1$ are the average Hamiltonians for the phase error-, phase transient-, pulse flip error-, and RF inhomogeneity-offset cross terms respectively.

	Sequence A (Fig. 1b)	Sequence B (Fig. 1c)
$\bar{H}_o^0$	0	0
$\bar{H}_D^0$	$-\frac{1}{2}\omega_D(I_+^1 I_+^2 - I_-^1 I_-^2)$	$-\frac{1}{2}\omega_D(I_+^1 I_+^2 - I_-^1 I_-^2)$
$\bar{H}_\delta^0$	$\frac{4}{t_c}(\delta_{\bar{x}} - \delta_x)I_x$	$\frac{4}{t_c}(\delta_{\bar{x}} - \delta_x)I_x$
$\bar{H}_\varepsilon^0$	0	0
$\bar{H}_p^0$	0	0
$\bar{H}_T^0$	0	0
$\bar{H}_D^1$	0	0
$\bar{H}_o^1$	0	0
$\bar{H}_\delta^1$	0	0
$\bar{H}_\varepsilon^1$	0	0
$\bar{H}_p^1$	$\frac{2}{t_c}(\phi_{\bar{x}}^2 - \phi_x^2)I_x$	$\frac{2}{t_c}(\phi_{\bar{x}}^2 - \phi_x^2)I_x$
$\bar{H}_T^1$	0	0
$\bar{H}_{\delta D}^1$	$2\omega_D(\delta_x + \delta_{\bar{x}})(I_y^1 I_z^2 + I_z^1 I_y^2)$	0
$\bar{H}_{\varepsilon D}^1$	$4\omega_D\varepsilon(I_y^1 I_z^2 + I_z^1 I_y^2)$	0
$\bar{H}_{PD}^1$	$\omega_D \frac{2\tau - \alpha}{2\tau}(\phi_x + \phi_{\bar{x}})(I_x^1 I_y^2 + I_y^1 I_x^2)$	$\omega_D \frac{2\tau - \alpha}{2\tau}(3\phi_x - \phi_{\bar{x}})(I_x^1 I_y^2 + I_y^1 I_x^2)$

	Sequence A (Fig. 1b)	Sequence B (Fig. 1c)
$\bar{H}_{TD}^1$	$-\omega_D \frac{2\tau-\alpha}{2\tau} J_2(I_x^1 I_y^2 + I_y^1 I_x^2)$	$-\omega_D \left[\frac{2\tau-\alpha}{2\tau} J_2(I_x^1 I_y^2 + I_y^1 I_x^2) + \frac{2\tau-2\alpha}{2\tau} J_1(I_x^1 I_z^2 + I_z^1 I_x^2) \right]$
$\bar{H}_{DO}^1$	0	$-c\omega_D \frac{(2\tau-\alpha)(4\tau-\alpha)}{2\tau} (I_x^1 I_z^2 + I_z^1 I_x^2)$
$\bar{H}_{TO}^1$	0	0
$\bar{H}_{PO}^1$	0	0
$\bar{H}_{\varepsilon O}^1$	$\frac{c\varepsilon(2\tau-\alpha)}{3\tau} (I_z)$	$-\frac{c\varepsilon(2\tau-\alpha)}{3\tau} (I_z)$
$\bar{H}_{\delta O}^1$	$\frac{c(2\tau-\alpha)}{6\tau} (\delta_x + \delta_x^-) (I_z)$	$\frac{c(2\tau-\alpha)}{6\tau} (\delta_x - 3\delta_x^-) (I_z)$

Table 8

The number of coupled spins N measured in experiments using adamantane, in the presence of a pulse flip error, as described in the text. The error in N is propagated from the standard error of the fit of the coherence order distribution to a Gaussian function.

Pulse error	Sequence A	Sequence B
None (baseline)	106 ± 9	113 ± 9
94.5° pulses	71 ± 8	110 ± 9
104° pulses	3.0 ± 0.4	38 ± 6
113° pulses	1.9 ± 0.2	2.4 ± 0.5

Table 9

A comparison of the ratios of the magnitudes of various coherence orders obtained in experiments using adamantane in the presence of pulse flip errors. Each column is referenced to the baseline $4.0\ \mu\text{s}$ (90°) pulse case and each respective ratio for the baseline sequence has been normalized to unity.

Pulse sequence	ratio 2/0	ratio 1/2	ratio 4/2	ratio 10/2
A baseline	1	1	1	1
A 94.5° pulses	0.87	1.25	0.96	0.80
A 104° pulses	0.39	26	0.89	0.60
A 113° pulses	0.20	137	1.0	0.80
B baseline	1	1	1	1
B 94.5° pulses	1.0	0.99	0.99	0.97
B 104° pulses	0.6	4.5	0.97	0.61
B 113° pulses	0.31	1.7	1.4	1.1