Scaling and Time Reversal of Spin Couplings in Zero-Field NMR

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We report the observation of spin echoes resulting from the time reversal of isotropic many-body spin couplings in zero-field NMR. The coherent-averaging pulse sequences responsible for the scaling and the time reversal of isotropic interactions of first and second rank are based on cubic and icosahedral symmetry.

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Among the most extraordinary phenomena in nuclear magnetic resonance (NMR) is the spin echo [1]. Although the original spin echo and its analogs in other areas of spectroscopy [2] result from reversing the dephasing due to independent, "inhomogeneous" interactions, a true many-body spin echo resulting from a reversal of the (seemingly irreversible) decay due to "homogeneous" spin-spin couplings has been demonstrated [3]. The phenomenon occurs in high magnetic field and can be thought of as arising from a reversal of the sign of the Hamiltonian describing the *truncated* spin-spin couplings [4], thereby reversing the evolution of the spins. Such time-reversal effects, induced by coherent averaging under sequences of radio-frequency pulses [5], have made possible a number of novel experiments including *selective* excitation of n-quantum transitions [6].

An interesting question is whether the high magnetic field normally present in NMR experiments is essential to the possibility of time reversal of the spin-spin couplings. Could such experiments be done in zero-field NMR, where there is no truncation or privileged direction and the full, untruncated, Hamiltonian is responsible for the decay of spin order [7]? In this Letter, we show theoretical and experimental results involving general schemes of coherent averaging in zero field using dc magnetic-field pulse sequences that conform to cubic and icosahedral symmetry. From these schemes emerges the possibility of scaling, decoupling, and time reversal in zero field.

The most general constraint that we impose upon coherent-averaging schemes in zero field is that the energy levels of the coherently averaged local interactions remain "zero-field-like," i.e., independent of the orientation of the sample with respect to the laboratory frame. Although there may be some privileged directions in the laboratory frame, along which the dc magnetic-field pulses are applied, for instance, the overall effect of the process must be independent of the orientation of the local interaction axis with respect to these directions. The process or the sequence is then called *isotropic*. It can be shown that isotropic processes are reduced to the *scaling* of the local interactions, i.e., multiplication by k, a constant scaling factor. For a given isotropic sequence, the scaling factors may not be identical for all types of interactions: heteronuclear or homonuclear, first rank (due to couplings with residual external fields, for example) or second rank (due to quadrupolar or dipole-dipole couplings). We shall focus on the simple but important case of *homonuclear* interactions of *first* and *second* ranks, where the scaled couplings are obtained as the *zero-order* average Hamiltonian over a coherent-averaging pulse sequence. The scaling factors for the first- and second-rank tensors will be denoted k_1 and k_2, respectively. For example, decoupling sequences have either k_1 or k_2 equal to zero, while for time-reversal sequences k_1 or k_2 is less than zero. A cubic-group-based theory has been published for some zero-field decoupling sequences [8]. Some spin interaction terms in high-field decoupling sequences can also be described as randomly oriented first-rank tensors, and iterative maps were designed according to a similar formalism based on cubic symmetries [9].

In zero field, the spin interactions are coherently manipulated by applying magnetic-field pulses, traditionally called "dc pulses" [8]. These pulses *rotate* the full zero-field Hamiltonian, and, for a given rank of interactions, their effect can be written in terms of Wigner matrices. A linear combination of Wigner matrix elements acts as the transformation relating the zero-order average Hamiltonian to the free zero-field Hamiltonian, implying that the condition for isotropy is

$$\langle D^l_{mm'}(R_i)\rangle_i = k_l \delta_{mm'}, \tag{1}$$

where $\langle\ \rangle_i$ is the average over i, and the $R_i=(\omega_i,\mathbf{n}_i)$ are the rotations applied to the spin Hamiltonian, defined by the net rotation angles ω_i and the rotation-axis orientations $\mathbf{n}_i$. By taking the trace of both sides of (1), it is found that the scaling factor is related only to the characters of the Wigner matrices, which are independent of the $\mathbf{n}_i$ [10]:

$$k_l = \langle \chi_l(\omega_i)\rangle_i/(2l+1). \tag{2}$$

For $l=1$ and 2,

$$k_1 = \langle (2\cos\omega_i - 1)/3\rangle_i, \tag{3a}$$

$$k_2 = \langle (4\cos^2\omega_i + 2\cos\omega_i - 1)/5\rangle_i. \tag{3b}$$

The scaling factors depend only on the *mean* and the *mean square* of $\cos\omega$ during the irradiation period.

Equations (3) restrict k_1 and k_2 to the shaded region of the (k_1,k_2) plane shown in Fig. 1, with $-\frac{1}{3} \le k_1 \le 1$ and $-\frac{1}{4} \le k_2 \le 1$. For sequences that are isotropic for one rank (but not necessarily for the other) the limits on scaling factors still hold.

Whereas the scaling factors depend only on the ω_i, the condition of isotropy also constrains the $\mathbf{n}_i$. A wide range of solutions is allowed, some of the simplest based on group-symmetry arguments. Equation (1) can be decomposed into irreducible representations of SO(3), yielding ranks $\lambda = 0-2l$ [10]. Thus, for both first- and second-rank interactions, icosahedral distributions of $\mathbf{n}_i$ readily satisfy (1) and generate isotropic sequences (the icosahedral symmetry averages out all terms from $\lambda = 1$ to 4) [11]. For example, in "zero-field NMR in high field" [12], contiguous magnetic pulses of net rotation $2n\pi$ applied along the fivefold axes of an icosahedron provide an isotropic scaling by $(k_1,k_2) = (\frac{1}{3}, \frac{1}{5})$ as shown by point E in Fig. 1. In practical applications, it is much more convenient to use sequences based on cubic symmetries (i.e., involving only $\pi/2$ pulses along x, y, and z) [8]. Thus, the R_i are chosen among the 24 rotations of the cubic group, and combined to yield isotropic sequences. However, the range of accessible scaling factors reduces as compared with the general limits given by (3) [13]. For instance, the optimum time-reversal scaling reduces from $-\frac{1}{4}$ to $-\frac{1}{5}$ in the cubic cases (points D and F in Fig. 1).

Decoupling sequences occur when a scaling factor vanishes, and the isotropic scaling formalism predicts that rank-selective decoupling can be achieved between first- and second-rank interactions (regions A and B in Fig. 1). An example, using icosahedral symmetry, is provided by the following sequence:

$$([\tau - \pi_i - 3\tau - \pi_i]_{i=1,6})_n , \tag{4}$$

which decouples first-rank interactions while scaling the second-rank interactions by $\frac{2}{5}$. All of these pulses are along the six fivefold axes of an icosahedron, labeled by i, and are of nutation angle π. Indeed, this sequence removes line broadening due to the coupling with residual inhomogeneous fields of the zero-field spectrometer. Decoupling of second-rank dipole-dipole interactions in zero field (not isotropic for first rank) can be achieved by a sequence of twelve $\pi/2$ pulses along the x, y, and z directions [8]. Experimental application of such a sequence narrowed the proton NMR spectrum of solid adamantane from 15 kHz to 500 Hz in zero field [13].

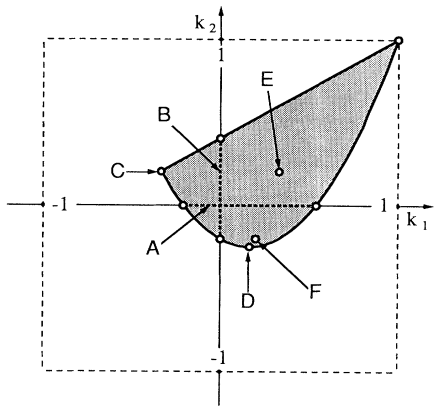

FIG. 1. Allowed combinations of isotropic scaling factors for first- ($l=1$) and second- ($l=2$) rank interactions, k_1 and k_2, are restricted to the shaded region of the (k_1,k_2) plane. As explained in the text, some combinations are of particular interest in applications: A, line from $(k_1 = (1-\sqrt{5})/6,\ k_2 = 0)$ to $((1+\sqrt{5})/6, 0)$, scaling of $l=1$ with decoupling of $l=2$ interactions (zero-field analog of Waugh-Hu-Ha [5]); B, line from $(0, -\frac{1}{5})$ to $(0, \frac{2}{5})$, scaling of $l=2$ with decoupling of $l=1$ interactions; C, $(-\frac{1}{3}, \frac{1}{5})$, optimal time reversal for $l=1$ interactions; D, $(\frac{1}{6}, -\frac{1}{4})$, optimal time reversal for $l=2$ interactions; E, $(\frac{1}{3}, \frac{1}{5})$, scaling factors for "zero-field NMR in high field" [12]; F, $(\frac{1}{5}, -\frac{1}{5})$, optimal time-reversal scaling for $l=2$ interactions under sequences involving only $\pi/2$ pulses along x, y, and z.

Of particular interest is the possibility of time reversal of first- and second-rank interactions. Optimal time reversal for first rank (maximum $-k_l = \frac{1}{3}$) is obtained by the following sequence of tetrahedral symmetry:

$$\pi_x - (\tau - \pi_y - \tau - \pi_x - \tau - \pi_z)_n - \pi_{-x} . \tag{5}$$

This sequence is not isotropic for second-rank interactions. It can, however, be made isotropic in second rank by adding $\pi/2$ pulses producing scaling factors of $k_1 = -\frac{1}{3}$ and $k_2 = \frac{1}{5}$ (point C in Fig. 1). The adapted sequence is

$$\pi_x - [\tau - (\pi/2)_y - 4\tau - (\pi/2)_y - \tau - (\pi/2)_x - 4\tau - (\pi/2)_x - \tau - (\pi/2)_z - 4\tau - (\pi/2)_z - \tau - (\pi/2)_{-y} - 4\tau - (\pi/2)_{-y} - \tau - (\pi/2)_{-x} - 4\tau - (\pi/2)_{-x} - \tau - (\pi/2)_{-z} - 4\tau - (\pi/2)_{-z}]_n - \pi_{-x} . \tag{6}$$

The time-reversal sequence (5) was demonstrated on the proton NMR of a liquid water sample in an inhomogeneous residual field generated by deliberately setting the zero-field shimming coils away from their optimal values. The residual field varied in both magnitude and orientation over the sample. To observe the effect of time reversal, we generated an echo, as shown in Fig. 2. The decay of the signal was monitored under free evolution in the inhomogeneous field, up to some time t, where the sequence was applied. At time $4t$, an echo was recovered from the depolarized sample, showing the time-reversal effect with a $\frac{1}{3}$ scaling factor. A secondary echo was also obtained by further application of the sequence followed by a free evolution. In contrast with the original Hahn echo in high-field NMR, the time reversal of first-rank

tensors cannot be performed in zero field by application of a single pulse. The Hahn echo performs a phase conjugation that is generated with one rotation because of the pseudo-two-dimensional behavior of the system in high field. In three dimensions, however, a phase conjugation cannot be reduced to a single rotation, although combinations of pulses can generate an inversion.

Time reversal for second-rank interactions ($k_2 = -\frac{1}{5}$ scaling) is given by the sixteen-pulse sequence

$$(\pi/2)_{-x}\text{-}(\pi/2)_{-y}\text{-}[\tau\text{-}(\pi/2)_x\text{-}\tau\text{-}(\pi/2)_y\text{-}\tau\text{-}(\pi/2)_x\text{-}2\tau\text{-}(\pi/2)_x\text{-}\tau\text{-}(\pi/2)_{-y}\text{-}\tau\text{-}(\pi/2)_x\text{-}\tau\text{-}(\pi/2)_y\text{-}2\tau\text{-}(\pi/2)_y\text{-}\tau\text{-}(\pi/2)_{-x}\text{-}\tau\text{-}(\pi/2)_{-y}\text{-}\tau\text{-}(\pi/2)_{-x}\text{-}2\tau\text{-}(\pi/2)_{-x}\text{-}\tau\text{-}(\pi/2)_y\text{-}\tau\text{-}(\pi/2)_{-x}\text{-}\tau\text{-}(\pi/2)_{-y}\text{-}2\tau\text{-}(\pi/2)_{-y}]_n\text{-}(\pi/2)_y\text{-}(\pi/2)_x\,. \quad (7)$$

This sequence isotropically scales first-rank interactions by $k_1 = +\frac{1}{5}$ (point F in Fig. 1). In this process, the Hamiltonian is rotated by all of the six $\pi/2$ and the eight $3\pi/2$ rotations of the cubic group, with relative weights 2 to 1, respectively [13]. The time reversal of zero-field dipolar couplings using sequence (7) was demonstrated on a sample of solid adamantane, generating an echo after the free induction decay, as shown in Fig. 3. This echo sequence is an isotropic, zero-field analog of the "magic sandwich" in high field [3]. As for first-rank interactions, a secondary echo was also obtained by further application of the sequence followed by a free evolution.

The experiments were carried out on a modified version of our zero-field spectrometer [14]. The sample polarization was prepared and monitored using field cycling with a sample shuttling system [7,14], and the zero-field evolution was initiated and terminated by the sudden switching of a magnetic field (along the main z axes) stronger than the local interactions [7]. Three class-A, dc to 1 MHz, 2-kW amplifiers were interfaced to the 0.1-μs-resolution pulse programmer via 12-bit digital-to-analog converters. They provided up to 75×10^{-4} T in three orthogonal coils, x, y, and z, around the zero-field region of the spectrometer. The homogeneity and the orthogonality of the coils over the sample (0.6 mm diameter and 0.7 mm height) were better than 0.5%. Pulse precision and stability had to be especially addressed because symmetrizations to compensate for first-order average Hamiltonian and for finite pulse lengths [4] increased the recycling times by at least a factor of 6. These symmetrized sequences were produced by first repeating the basic series of pulses in opposite order with the opposite sign, and then this doubled sequence was repeated with the pulse directions permuted [9]. The corrections yielded significant improvements although the complete se-

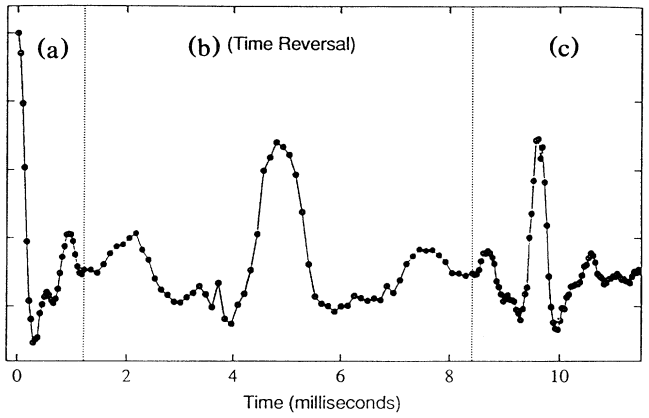

FIG. 2. Isotropic spin echoes on first-rank interactions: (a) The magnetization of the protons in a sample of water decays in the low residual magnetic field (which varies in both direction and magnitude over the sample) in the zero-field NMR spectrometer. (b) The isotropic time-reversal sequence (5) is applied after 1.2 ms of free evolution, and generates an echo 3.6 ms later, because the scaling factor is $-\frac{1}{3}$. (c) Free evolution is resumed at time 8.4 ms, resulting in a second echo at 9.6 ms. One sample point is taken per cycle (120 μs). The pulse duration is 2 μs.

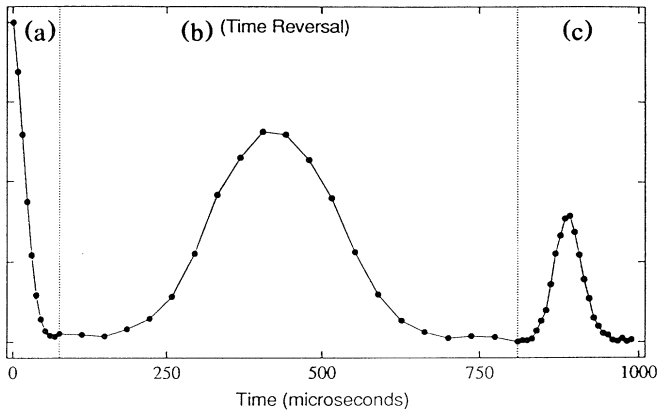

FIG. 3. Isotropic spin echoes for zero-field second-rank interactions. (a) The magnetization of the protons in polycrystalline adamantane decays due to the local isotropic dipole-dipole couplings. (b) After 74 μs, the isotropic time-reversal sequence (7) is applied and the magnetization is retrieved 370 μs later, because the scaling factor is $-\frac{1}{5}$. (c) Free evolution in zero field is resumed at time 810 μs, resulting in a second echo at 883 μs. One sample point is taken per cycle (36.8 μs). The pulse duration is 1 μs.

quences commonly reached hundreds of pulses.

The theoretical and experimental examples described above show the feasibility of isotropic coherent irradiation experiments in zero-field NMR. Sequences for selective decoupling of first-rank interactions can improve the resolution when limited by arbitrary residual fields, and provide a starting point for treating the problem of zero-field heteronuclear decoupling (because heteronuclear interactions are first-rank tensors in each of the spin species). Particularly interesting is the possibility of using time reversal to perform "multipolar zero-field NMR," the isotropic analog of high-field multiple-quantum NMR [6]. This experiment can provide a new tool for structural studies by using isotropic dipole-dipole couplings to extract structural information even in polycrystalline samples.

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