

Filters for long-lived spin order

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Abstract

Nuclear magnetic equivalence symmetry is a key property in the ability of a molecule to sustain long-lived spin order. In addition, it is an important property in the ability to distinguish NMR signals of long-lived spin order from those due to other types of spin order. This chapter presents a general view of the symmetry properties of long-lived spin order including symmetry under rotations in three dimensional space. Long-lived spin order is found to be a type of “scalar” spin order, invariant to global rotations of nuclear spin systems. Schemes for filtering scalar order of progressive complexity, and their applications in NMR of long-lived spin order, are then discussed.

1 Introduction

The methodology of preserving nuclear magnetic order away from thermal equilibrium for durations beyond the T_1 limit has seen development on several fronts in these past years. First is the design of molecules that exhibit long-lived nuclear spin order and the conditions under which this order may be sustained[1]. Second are the pulse sequences that convert long-lived spin order to and/or from observable magnetization[2, 3, 4]. Progress in these areas is extensive and has been summarized periodically in the above review articles as well as in other chapters of this book. The present chapter intends to survey a (third) smaller but nonetheless important area, concerning how to distinguish long-lived nuclear spin order from other types of order. To outline this methodology and its motivation one may consider the sequence illustrated in Figure 1a, which generalizes how long-lived order can be detected via an NMR experiment. Throughout the sequence, the state of the nuclear spin system is represented in the usual Liou-villian formalism[5, 6] by a density operator $|\rho\rangle$ where $\text{Tr}(\rho^\dagger\rho) = 1$. An initial state $|\rho\rangle = |\rho_{\text{init}}\rangle$ is subject to an experimental pulse sequence, whose effect is represented by a unitary superoperator \hat{U} , that may partly or wholly transform $|\rho_{\text{init}}\rangle$ into a detectable form of magnetization represented by $|Q_{\text{obs}}\rangle$. The time-domain signal $s(t)$ that arises is then proportional to the scalar product

$$s(t) = \text{Tr}(Q_{\text{obs}}^\dagger \hat{U}_{\text{obs}}(t) \hat{U} \rho_{\text{init}}), \quad (1)$$

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where \hat{U}_{obs} is the propagator during the detection period.

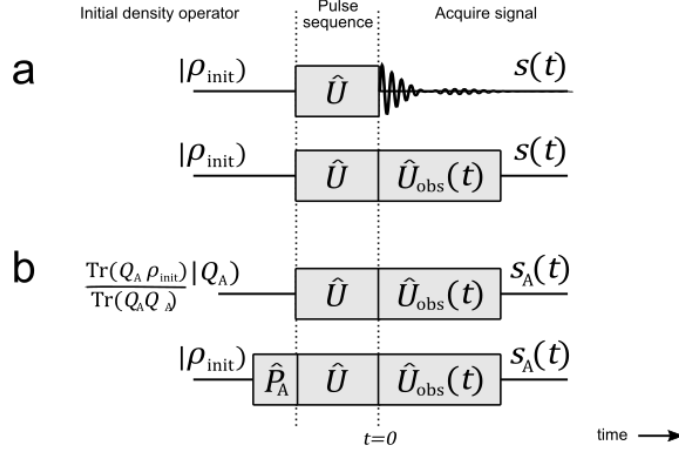


Figure 1: Pulse sequence diagrams illustrating the concept of signal filtering in NMR, using Liouville space notation: (a) the initial density operator $|\rho_{\text{init}}\rangle$ is converted to an observable signal, without filtering; (b) A filtered version of $|\rho_{\text{init}}\rangle$, via projection superoperator \hat{P}_A , produces only the portion of the signal that originates from spin order corresponding to an operator Q_A .

In many NMR experiments it is desirable to find the component of $s(t)$, let us say $s_A(t)$, originating from a specific type of spin order $|Q_A\rangle$ in $|\rho_{\text{init}}\rangle$. The amplitude of s_A is proportional to the fraction of $|Q_A\rangle$ within $|\rho_{\text{init}}\rangle$ and therefore is a route to detect higher spectroscopic dimensions as well as detect so-called “dark” spin order that is not directly observable. Of course, the latter includes long-lived spin order, which carries no overall magnetization. To achieve this objective it would be convenient to introduce into the experimental sequence a way of substituting the initial spin density operator $|\rho_{\text{init}}\rangle$ by the desired order, $|Q_A\rangle$. In other words, a method of “filtering” Q_A from unwanted terms in $|\rho_{\text{init}}\rangle$ is needed.

In the Liouvillian formalism, such a filter is found by applying a projection superoperator, \hat{P}_A , whose representation equals the self outer-product of the normalized operator $|Q_A\rangle$: $\hat{P}_A = |Q_A\rangle\langle Q_A|/\text{Tr}(Q_A^\dagger Q_A)$ [5]. The projection superoperator yields a signal component $s_A(t)$ when applied before \hat{U} as illustrated in Figure 1b and seen below:

$$s_A(t) = [1/\text{Tr}(Q_A^\dagger Q_A)] \text{Tr}(Q_{\text{obs}}^\dagger \hat{U}_{\text{obs}}(t) \hat{U} Q_A) \text{Tr}(Q_A^\dagger \rho_{\text{init}}); \quad (2)$$

$$= \frac{\text{Tr}(Q_A^\dagger \rho_{\text{init}})}{\text{Tr}(Q_A^\dagger Q_A)} s(t). \quad (3)$$

This chapter concerns the questions of whether \hat{P}_A can be realized experimentally when $|Q_A\rangle$ is the long-lived spin order of the system, and if so, how it is constructed. The answer to the first question is yes, it is possible to construct

projection superoperators that isolate the NMR signals originating from long-lived spin order. For the second question there are several options available, which may be classed in one of the following categories:

1. Single-scan filters – a pulse sequence whose superoperator representation is equal or approximate to P_A , allowing the filter to be implemented during a single NMR acquisition.
2. Multi-scan filters – a set of pulse sequences whose superoperators add together to equal or approximate P_A .

As a brief note on the difference between the two categories, single-scan filters are preferred where time saving is important or where the initial experimental conditions cannot be reproduced accurately over multiple scans – for instance during an irreversible chemical reaction, a spin hyperpolarization procedure, or other time-dependent process. Single-scan filters must correspond to non-unitary superoperators, however. These are not guaranteed to exist for any arbitrary spin system. The multi-scan filter concept, on the other hand, is based on an approach where \hat{P}_A is constructed by a linear superposition of unitary operators that have well known symmetry properties. These may include rotation operators, which can be applied about almost any axis by modern Fourier-transform NMR hardware via phase-shifted radiofrequency pulses[7]. The advantage of multiple-scan filters is a much more general applicability, though at the expense of a longer experiment duration.

Section 2 of this chapter reviews symmetries of long-lived spin order, in order to formalize the method for constructing the projection superoperator \hat{P} that is presented in Section 3. Applications are discussed in Section 4.

2 Symmetry properties of long-lived spin order

2.1 Spin permutation symmetry

Long-lived spin order may arise in molecules that contain two or more coupled nuclei under conditions of intrinsic[8, 9], imposed[10, 11] or approximate[12, 13] magnetic equivalence. This includes the simplest diatomic molecule, hydrogen ($^1\text{H}_2$), where the nuclei of both atoms have spin quantum number $I = 1/2$. The four nuclear Zeeman states of the H_2 molecule can be mixed to form a new state basis containing one singlet state,

$$|S_0\rangle = (|\alpha_1\beta_2\rangle - |\beta_1\alpha_2\rangle)/\sqrt{2}, \quad (4)$$

and a triplet state

$$|T_{+1}\rangle = |\alpha_1\alpha_2\rangle \quad (5)$$

$$|T_0\rangle = (|\alpha_1\beta_2\rangle + |\beta_1\alpha_2\rangle)/\sqrt{2} \quad (6)$$

$$|T_{-1}\rangle = |\beta_1\beta_2\rangle. \quad (7)$$

The singlet and triplet are eigenstates under an operation of permuting the nuclear labels. Adopting notation where ‘(12)’ denotes this operation, and the

numbers ‘1’ and ‘2’ signify the nuclear labels given in subscripts above, the property is summarized as:

$$(12)|S_0\rangle = -|S_0\rangle; \quad (8)$$

$$(12)|T_m\rangle = +|T_m\rangle; \quad \text{for } m = -1, 0 \text{ and } +1. \quad (9)$$

Since $(12)^2 = (12)(12)$ is an identity operation, it follows that the singlet and triplet states are an eigenbasis of the symmetry group that comprises the element ‘(12)’ and the identity operator. Formally this group is called the molecular symmetry group S_2 . The triplet owes its name to the trio of symmetric eigenstates, each of character +1 under (12), while the singlet state is the lone eigenstate that transforms antisymmetrically under (12), with a character of -1 .

Long-lived spin order in spin-1/2 pairs requires that the nuclear spin Hamiltonian transforms as a totally symmetric irreducible representation under operations of the molecular symmetry group. This condition equates to a selection rule where different irreducible representations of a group cannot be mixed by interactions that transform as the totally symmetric irreducible representation of the same group. A population imbalance between the singlet and triplet therefore cannot tend towards equilibrium, and formally known as “decoherence-free” spin order, but in practice always decays and is termed “long-lived” spin order[14, 15]. The normalized operator corresponding to this spin order is

$$Q_{\text{LLS}}^{\text{ST}} = |S_0\rangle\langle S_0| - \frac{1}{3}(|T_{-1}\rangle\langle T_{-1}| + |T_0\rangle\langle T_0| + |T_{+1}\rangle\langle T_{+1}|), \quad (10)$$

where the subscript ‘LLS’ denotes “long-lived spin order”.

The same principles of nuclear permutation symmetry can be applied to analyze a spin system of three magnetically equivalent ^1H nuclei in a methyl (CH_3) group, e.g. acetic acid (CH_3COOH) or toluene ($\text{CH}_3\text{C}_6\text{H}_5$). The appropriate molecular symmetry group S_3 is isomorphic with the point group C_{3v} . Like the $^1\text{H}_2$ diatomic, the three-spin-1/2 eigenstates are also partitioned into two types of symmetry species. The Zeeman product states are superposed to give four totally symmetric states with label ‘A’ and total nuclear spin quantum number $I = 3/2$ plus two sets of doubly degenerate states with symmetry label ‘E’ and total spin quantum number $I = 1/2$:

$$|A_{+3/2}\rangle = |\alpha_1\alpha_2\alpha_3\rangle, \quad (11)$$

$$|A_{+1/2}\rangle = (|\alpha_1\alpha_2\beta_3\rangle + |\alpha_1\beta_2\alpha_3\rangle + |\beta_1\alpha_2\alpha_3\rangle)/\sqrt{3}, \quad (12)$$

$$|A_{-1/2}\rangle = (|\alpha_1\beta_2\beta_3\rangle + |\beta_1\alpha_2\beta_3\rangle + |\beta_1\beta_2\alpha_3\rangle)/\sqrt{3}, \quad (13)$$

$$|A_{-3/2}\rangle = |\beta_1\beta_2\beta_3\rangle \quad (14)$$

$$|E_{+1/2}^{(a)}\rangle = (|\alpha_1\alpha_2\beta_3\rangle + \epsilon|\alpha_1\beta_2\alpha_3\rangle + \epsilon^*|\beta_1\alpha_2\alpha_3\rangle)/\sqrt{3}, \quad (15)$$

$$|E_{-1/2}^{(a)}\rangle = (|\alpha_1\beta_2\beta_3\rangle + \epsilon|\beta_1\beta_2\alpha_3\rangle + \epsilon^*|\beta_1\alpha_2\beta_3\rangle)/\sqrt{3}, \quad (16)$$

$$|E_{+1/2}^{(b)}\rangle = (|\alpha_1\alpha_2\beta_3\rangle + \epsilon^*|\alpha_1\beta_2\alpha_3\rangle + \epsilon|\beta_1\alpha_2\alpha_3\rangle)/\sqrt{3}, \quad (17)$$

$$|E_{-1/2}^{(b)}\rangle = (|\alpha_1\beta_2\beta_3\rangle + \epsilon^*|\beta_1\beta_2\alpha_3\rangle + \epsilon|\beta_1\alpha_2\beta_3\rangle)/\sqrt{3}, \quad (18)$$

where $\epsilon = \exp(-2\pi i/3)$. The A manifold and E manifold correspond to different irreducible representations of the S_3 group and the A symmetry label indicates the totally symmetric irreducible representation. Therefore, if the spin system Hamiltonian transforms as the totally symmetric A representation of the group, transitions between A/E manifolds are forbidden. The population difference between the A manifold and E manifolds corresponds in this case to long-lived spin order given by:

$$Q_{\text{LLS}}^{\text{AE}} = \sum_{m_a=-3/2}^{3/2} |A_{m_a}\rangle\langle A_{m_a}| - \sum_{m_e=-1/2}^{1/2} (|E_{m_e}^{(a)}\rangle\langle E_{m_e}^{(a)}| + |E_{m_e}^{(b)}\rangle\langle E_{m_e}^{(b)}|). \quad (19)$$

The symmetry group of the relaxation Hamiltonian for CH_3 is determined by the rate of rotation with respect to the rest of the molecule. It turns out that a methyl group that does not internally rotate cannot support long-lived states, since the three pairwise internuclear dipole-dipole couplings transform collectively as a mixture of A and E irreducible representations. Only in the limit of fast internal rotation is the E part averaged out, leaving the totally symmetric A representation, which cannot mix the symmetry species. Experiments have shown that A–E population imbalances are long-lived in molecules with very low energy barriers to methyl rotation, including picoline and other methylated aromatic rings[16].

The long-lived spin order described in Equations 10 and 19 may appear quite different as written in the eigenbasis of the permutation symmetry group. However, they are very similar when represented in the basis of spin product operators. It is seen that both involve a type of two-spin product order, namely:

$$Q_{\text{LLS}}^{\text{ST}} \equiv I_1 \cdot I_2; \quad (20)$$

$$Q_{\text{LLS}}^{\text{AE}} \equiv (I_1 \cdot I_2 + I_2 \cdot I_3 + I_3 \cdot I_1)/3; \quad (21)$$

where $I_j = \{I_{jx}, I_{jy}, I_{jz}\}$ and $I_j \cdot I_k = I_{jx}I_{kx} + I_{jy}I_{ky} + I_{jz}I_{kz}$. In NMR jargon this type of order is also called “scalar order”, because each term is the scalar product of two vector spin operators.

2.2 Rotation symmetry in three-dimensional space

Spherical tensor operators[7] are commonly applied in the theoretical treatment of NMR systems with rotational symmetry, including solid-state NMR and NMR relaxation. Each spherical tensor basis operator, denoted $|T_{lm}\rangle$, has definitive properties of three-dimensional rotation and for this reason, is a useful basis to represent Q_{LLS} . For the purpose of this chapter, it is sufficient to know that two quantum numbers are needed to completely describe the transformation properties of spin order under a global rotation of the spin system, namely the unitary transformation where each nucleus is rotated by the same angle about the same axis. The principal index ‘ l ’ or ‘rank’ of the tensor operator is an integer $l \geq 0$ that indicates the number of angular nodes when the spin operator is rotated about an axis at right angles to the spin quantization axis.

The second index ‘ m ’ is also an integer, which indicates the coherence order of the spherical tensor operator and has value $0 \leq m \leq l$. The expression

$$\hat{R}_{zyz}(\alpha, \beta, \gamma)|T_{lm}\rangle = \sum_{m'=-l}^l \exp(-i[m\alpha + m'\gamma])d_{mm'}^l(\beta)|T_{lm'}\rangle \quad (22)$$

summarizes these properties and moreover that any a given spherical tensor operator transforms under rotation into a linear superposition of other operators from the same rank. Here \hat{R}_{zyz} denotes a rotation superoperator in the zyz convention [5, 7], where α , β and γ are the corresponding Euler angles of rotation and d^l is the $(2l+1) \times (2l+1)$ -rank block of the Wigner-d matrix[17]. Each tensor of rank l is an irreducible representation of the three-dimensional rotation group $SO(3)$. For more advanced detail on spherical tensors, the reader should see Ref. [17] and other texts on the theory of quantized angular momentum.

The scalar spin order as defined above in Equations 20 and 21 is proportional to the spherical tensor operator $|T_{00}\rangle$:

$$Q_{\text{LLS}} \sim |T_{00}\rangle. \quad (23)$$

A check of the property $l = 0$ is how operators $I_j \cdot I_k$ in Equations 20+21 are independent of axes choice, in that they commute with the total angular momentum operator of the spin system $I_{\text{total},\xi} = \sum_j (I_j \cdot \xi)$ along any axis ξ in three-dimensional space: $[I_j \cdot I_k, I_{\text{total}}] = 0$.

Equation 23 is a result of major importance. It concisely summarizes the relationship between long-lived spin order and the rotational properties of the spin system, in particular that long-lived order is invariant to rotations applied globally to the nuclear spin system. While the conclusion is introduced here by observing only the very simplest systems, it also applies generally where $|Q_{\text{LLS}}\rangle$ transforms as the totally symmetric representation of the molecular symmetry group. For example, long-lived spin order in systems of four nuclei (e.g. $^{13}\text{C}_2$]-acetylene[18], citric acid[19] and aromatic rings[20, 21]) or system of three nuclei without chemical equivalence (e.g. acrylic acid [22]) also are superpositions of scalar spin order and are invariant to rotation in the same way. Equation 23 therefore provides crucial insight into the approach for filtering long-lived order, explained further in Section 3, and a promise that filtration methods are general rather than restricted to specific spin systems or pulse sequences.

3 Filter methods

3.1 General approach

The spherical tensor operator basis provides a complete set of orthonormal operators to represent the nuclear spin density operator, where the coefficient of each operator $|T_{lm}^j\rangle$ is equal to the projection $\text{Tr}(T_{lm}^{j\dagger}\rho)/\text{Tr}(T_{lm}^{j\dagger}T_{lm}^j)$:

$$|\rho\rangle = \sum_{j,l,m} \frac{(T_{lm}^j|\rho)}{(T_{lm}^j|T_{lm}^j)}|T_{lm}^j\rangle. \quad (24)$$

Here the label j is introduced to differentiate spin order of the same l and m involving specific nuclei within the spin system.

In the previous section it was deduced that long-lived spin order transforms as the totally symmetric irreducible representation of the rotation group. Therefore a filter that destroys all spin order of rank $l \geq 1$ is close to fulfilling the objective of a projection superoperator $\hat{P}_{\text{LLS}} = |Q_{\text{LLS}}\rangle\langle Q_{\text{LLS}}|/\text{Tr}(Q_{\text{LLS}}^\dagger Q_{\text{LLS}})$, which has yet to be found. For now we will examine this scalar order filtering approach, since in most cases it performs as well if not the same as \hat{P}_{LLS} . The only case where these approaches are formally equal occurs for a spin-1/2 pair system (e.g. $^1\text{H}_2$, $^{15}\text{N}_2\text{O}$ [23] or $\text{R}^{13}\text{CO}^{13}\text{COR}'$ [13]) where the only type of scalar spin order is singlet-triplet population difference order. In systems of more than two nuclei the approaches are not identical because not all scalar order is long lived. For instance, three spin-1/2 nuclei may support three distinct types of scalar product order – say $I_1 \cdot I_2$, $I_1 \cdot I_3$ and $I_2 \cdot I_3$ – but only a specific linear combination of these may correspond to long-lived order. However, if the participating nuclei are all chemically and magnetically equivalent, then $|Q_{\text{LLS}}\rangle$ is the only type of scalar spin order that can be populated via unitary pulse sequences. In this case both \hat{P}_{LLS} and the scalar filter approach also produce the same final density operator. These results suffice to motivate the approximate approach.

3.2 Filters based on the rotation group SO(3)

The great orthogonality theorem of group theory states that the projection of each symmetry element upon an irreducible representation of a group must always sum to zero and vanish, except in the case of the totally symmetric irreducible representation. When applied to the rotation group SO(3) – which has an infinite number of elements – the statement is given by the integral

$$\frac{1}{8\pi^2} \int_{\text{SO}(3)} \hat{R}(\alpha, \beta, \gamma) T_{lm}^{(j)} d\alpha \sin\beta d\beta d\gamma = \begin{cases} T_{00}^{(j)} & \text{for } l = 0 \\ 0 & \text{for } l > 0 \end{cases} \quad (25)$$

The result obtained is that spherical tensor operators of rank ($l \geq 1$) are averaged to zero while the rank-0 or scalar spin order accumulates.

This is a helpful starting point from which to find methods that filter scalar order using a finite and ideally small number of symmetry operations. It happens that Equation 25 can be approximated well by a finite sum of rotations. In choosing this method one must accept that not all ranks $0 < l < \infty$ can be averaged. However, this is not a matter of great concern since: (i) there is always a maximum rank of the spin system, which is determined by the number of nuclei in the spin system. For n coupled spin-1/2 nuclei there will be $(2I+1)n$ angular momentum states and the density operator contains up to n units of total angular momentum, so the maximum rank is only $l_{\text{max}} = n$; (ii) even in large spin systems, higher-rank spin order ($l > 3$) is slow to build up and rarely able to generate strong NMR signals due to its short lifetime.

A filter composed of a finite number ($N^{\mathcal{S}}$) of rotations can be applied over multiple NMR scans as illustrated in Figure 2a. The set of Euler rotation-angle triplets is called the ‘sampling set’: $\mathcal{S} = \{(\alpha_1, \beta_1, \gamma_1), (\alpha_2, \beta_2, \gamma_2),$

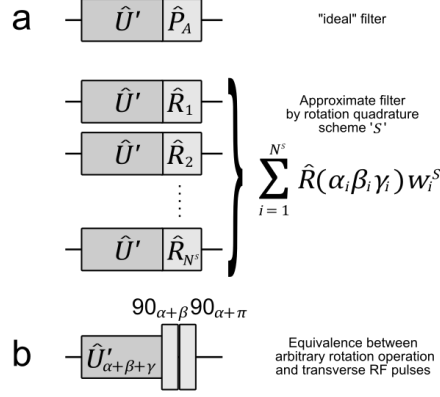


Figure 2: Rotation operations in signal filtering: (a) an ideal filter for spin order represented by $|Q_A\rangle$ is the projection superoperator \hat{P}_A , to be approximated by a finite sum of N^S rotations $\hat{R}_{zyz}(\alpha\beta\gamma)$; (b) Rotation about an arbitrary axis in the rotating frame of the spins can be produced by applying two 90-degree transverse rf pulses of appropriate phase plus applying a phase shift to all preceding elements \hat{U}' of the NMR pulse sequence[7, 24].

$(\alpha_{Ns}, \beta_{Ns}, \gamma_{Ns})\}$. The NMR experiment is repeated N^S times in which one of the rotations in \mathcal{S} is applied at the time point during the pulse sequence when the scalar order should be filtered, for instance using a pair of 90-degree pulses as shown in Figure 2b[7, 24]. By adding the NMR signals from all of the experiments, with appropriate weights, the signal components that derive from rank-0 spin order should accumulate constructively while those from higher ranks $l > 0$ should interfere destructively and sum to zero. For this procedure to be successful the Euler angles $(\alpha_i, \beta_i, \gamma_i)$ and weights w_i^S of the set \mathcal{S} must be chosen to satisfy the averaging property

$$\sum_{i=1}^{N^S} w_i^S \hat{R}_{zyz}(\alpha_i, \beta_i, \gamma_i) T_{lm}^{(j)} = \begin{cases} T_{00}^{(j)} & \text{for } l = 0 \\ 0 & \text{for } 1 \leq l \leq l_{\max} \end{cases} \quad (26)$$

where l_{\max} is the maximum accessible tensor rank of the spin system. If the weights are chosen to satisfy the property $\sum_{i=1}^{N^S} w_i^S = 1$, then the above condition can also be expressed using the Wigner matrix elements as

$$\sum_{i=1}^{N^S} w_i^S d_{mm'}^l(\beta_i) e^{-i2\pi(m\alpha_i + m'\gamma_i)} = \begin{cases} 1 & \text{for } l = 0, \\ 0 & \text{for } 1 \leq l \leq l_{\max} \end{cases} \quad (27)$$

Equation 27 sets out the averaging condition as a set of simultaneous equations. For a sampling set of size N^S there are generally $4N^S - 1$ unknowns that can be solved for (one weight and one Euler angle triplet per rotation). The number of simultaneous equations is equal to $1^2 + 2^2 + \dots + l_{\max}^2 = (l_{\max} + 1)(2l_{\max} + 1)(2l_{\max} + 3)/3$ and therefore increases with the cube of the number of spins

in the system. It is necessary for these equations to remain deterministic while reducing N^S as far as possible to minimize the experimental repetition. One may define λ_{\max}^S as the maximum rank which can be averaged by the sampling scheme. Then if $\lambda_{\max}^S \geq l_{\max}$, the filter can achieve its objective.

Fortunately, the number of constraints and therefore minimum value of N_S is bounded by a number far lower than the dimension of Equation 27 due to rotation, reflection and inversion symmetries in the Wigner matrix[17]. For example, all odd-rank tensor components ($l = \text{odd integer}$) can be averaged by using pairs of rotations where the Euler angles are (α, β, γ) and $(\alpha, \pi - \beta, \gamma)$. Some solutions are discussed below.

3.2.1 Polyhedral group filters

Finite rotation subgroups of $SO(3)$ include the tetrahedral (\mathcal{T} , Coxeter group $[3,3]^+$, $N^{\mathcal{T}} = 12$ rotation elements), octahedral (\mathcal{O} , Coxeter group $[4,3]^+$, $N^{\mathcal{O}} = 24$ rotation elements) and icosahedral (\mathcal{I} , Coxeter group $[5,3]^+$, $N^{\mathcal{I}} = 60$ rotation elements) groups. These can be shown to satisfy the averaging condition of Equation 27 with $\lambda_{\max} = 2, 3$ and 5 , respectively, using uniform weights $w_i^S = 1/N^S$ [25].

Euler angles for these rotation groups are given in Table 1. The α_i and β_i rotation angles are given by the azimuthal (ϕ) and polar (θ) angular coordinates of regular polyhedron vertices, e.g. tetrahedron with $\theta = \{0, \arccos[-1/3]\}$, $\phi = \{0, 2\pi/3, 4\pi/3\}$. To complete the Euler triplets, each vertex coordinate is joined by a γ rotation angle equal to the smallest n-fold rotation angle in the group, and multiples thereof until 2π , e.g. tetrahedron with n-fold rotations $\{0, 2\pi/3, 4\pi/3\}$. This algorithm equates to building up the operations of the rotation subgroup from its generating elements. The number of angles N^S is equal to the group order; for example \mathcal{O} has 6 vertex coordinates that are combined with 4 increments of $\pi/2$ around the circle, giving $N^{\mathcal{O}} = 24$.

In most cases, \mathcal{T} does a satisfactory job of filtering scalar order even when applied to spin systems that have a maximum spin rank of $l_{\max} > \lambda_{\max}^{\mathcal{T}} = 2$. Figure 3 demonstrates the tetrahedral filter applied to an aqueous solution of the amino acid L-phenylalanine. The molecule contains three adjacent alkyl protons whose resonances are shown in the spectrum of Figure 3a. The spectrum in Figure 3b(i) results from a pulse sequence designed to convert magnetization of the two C^β protons into scalar spin order of the kind $I_{H^{\beta 1}} \cdot I_{H^{\beta 2}}$ [26] and then to antiphase signal coherence before measurement. The line shape is a complicated mixture of contributions from scalar order, rank-1 spin order and higher ranks. A repeated measurement shown Figure 3b(ii) includes the tetrahedral filter to remove the contributions from the non-scalar spin order. A clean line shape is now recognizable in anti-phase. The residual peak at ~ 4.05 ppm is the result of two-spin scalar order of the type $I_{H^\alpha} \cdot I_{H^\beta}$ populated between H^α and H^β .

3.2.2 Phase cycling combined with field gradients

Polyhedral filters have advantages and disadvantages. One advantage is that they can be applied almost anywhere in the NMR pulse sequence by simply

\mathcal{S}	$N^{\mathcal{S}}$	α	β	γ	Eliminate spin order of rank					
					1	2	3	4	5	6
\mathcal{T}	12	0	0	$0, (2\pi/3)$ $(4\pi/3)$	✓	✓	✗	✗	✗	✗
		$2\pi/3$	$\arccos(-1/3)$							
		$4\pi/3$	$\arccos(-1/3)$							
		0	$\arccos(-1/3)$							
\mathcal{O}	24	0	0	$0, (\pi/2),$ $\pi, (3\pi/2)$	✓	✓	✓	✗	✓	✗
		0	$\pi/2$							
		$\pi/2$	$\pi/2$							
		π	$\pi/2$							
		$3\pi/2$	$\pi/2$							
		0	π							
\mathcal{I}	60	0	0	0 $(2\pi/5)$ $(4\pi/5)$ $(6\pi/5)$ $(8\pi/5)$	✓	✓	✓	✓	✓	✗
		0	$\arctan(2)$							
		$2\pi/5$	$\arctan(2)$							
		$4\pi/5$	$\arctan(2)$							
		$6\pi/5$	$\arctan(2)$							
		$8\pi/5$	$\arctan(2)$							
		$\pi/10$	$\pi - \arctan(2)$							
		$3\pi/10$	$\pi - \arctan(2)$							
		$5\pi/10$	$\pi - \arctan(2)$							
		$7\pi/10$	$\pi - \arctan(2)$							
		$9\pi/10$	$\pi - \arctan(2)$							
		0	π							

Table 1: Euler angles and spherical-rank averaging properties for the tetrahedral (\mathcal{T}), octahedral (\mathcal{O}) and icosahedral (\mathcal{I}) subgroups of $\text{SO}(3)$.

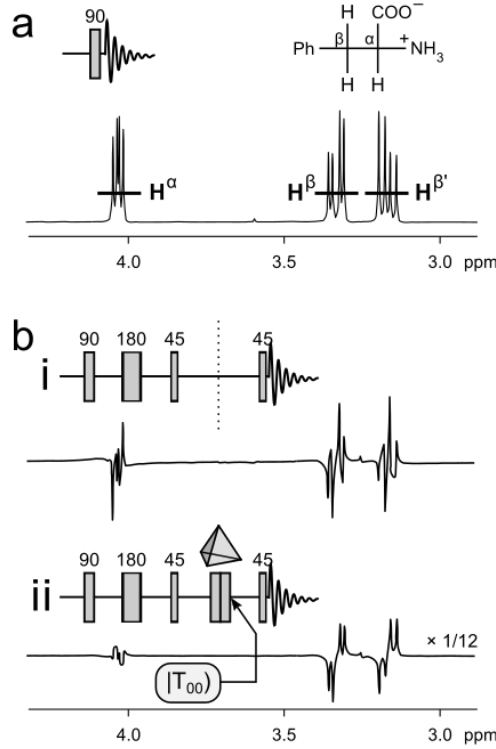


Figure 3: [Unpublished work by the author] ^1H NMR of phenylalanine in D_2O (5 mg / 500 μL): (a) single pulse-acquire spectrum at 9.4 T showing resonances in the aliphatic region; (b)(i) single-scan NMR signal after population of the singlet-triplet difference order, then reconversion to magnetization; (b)(ii) the same combined with a 12-step tetrahedral averaging cycle to isolate components of the signal that pass through scalar order.

introducing a couple of rf pulses and some rf phase cycling. Another potential advantage is that they exploit subgroups of $\text{SO}(3)$, which according to the orthogonality theorem allows them to isolate any rank of spin order, which is useful in other NMR contexts such as spin counting. The main disadvantage is a relatively large value of N^S versus maximum filter rank.

If we are only interested in scalar-order (rank-0) filters, it is possible to use a combination of pulsed field gradients and rf pulses to greatly reduce the minimum value of N^S needed to satisfy Equation 27. Field gradients provide an efficient means to dephase spin coherences. Spin dephasing in a gradient occurs due to the position-dependent phase shift applied to each type of spin order $|T_{lm})$ depending on its position in the sample (\mathbf{r}), the gradient field strength $G(\mathbf{r})$ and the coherence order m . In cases where the detected NMR signal is an average of the spin coherence across the whole sample, the gradient pulse effectively filters out the spin order with $|m| > 0$, leaving only spin order corresponding to

spherical tensor operators $|T_{l0})$.

The basic filter element shown in Figure 4a comprises a field gradient pulse, then a rotation of angle β about the y axis, then another gradient pulse. These gradients replace the need average over the α and γ Euler angles provided that coherence refocusing does not occur. The most reliable way to avoid refocusing is by applying the gradients along orthogonal spatial axes, which most commercial NMR instruments are equipped for. If there is only one available axis of field gradient, the strengths should be chosen to avoid the condition $G_{\text{before}}(\mathbf{r})/G_{\text{after}}(\mathbf{r}) = m'/m$. Assuming that the gradients adequately remove spin coherences with $m > 0$, then only the β angles and weights need to be solved for. The averaging condition now appears much simpler since there are $l_{\text{max}} + 1$ equations for a total of $2N^S - 1$ unknowns:

$$\sum_{i=1}^{N^S} w_i^S d_{00}^l(\beta_i^S) = \begin{cases} 1 & \text{for } l = 0 \\ 0 & \text{for } 1 \leq l \leq l_{\text{max}} \end{cases} \quad (28)$$

An elegant solution of Equation 28 is known and called Gauss-Legendre quadrature[27, 28]. For any integer value of N^S the set of β angles are set to the N^S zeroes of the Legendre polynomial function $P_{N^S}(\cos(\beta))$ where

$$P_{N^S}(\cos(\beta_i)) = 0 \quad (29)$$

and the corresponding weights are

$$w_i = \frac{\sin \beta_i}{\sum_{i=1}^{N^S} \sin \beta_i} \quad (30)$$

For a given value of N^S it is found $\lambda_{\text{max}} = 2N^S - 1$ and the cosine function is antisymmetric about $\beta = \pi/2$, all odd-integer spherical ranks automatically average to zero. Evidently the gradient pulses remove a lot of hard work from the filtering problem. Only two angles ($N^S = 2$) are needed to reach $\lambda_{\text{max}} = 3$ ($\beta = 54.74^\circ$ and 125.26° , weights = $1/2$ and $1/2$). Without gradients the same averaging property requires the octahedral (\mathcal{O}) filter, which has 12 times as many angles ($N^{\mathcal{O}} = 24$).

3.2.3 Magic angles

The pulse sequence illustrated in Figure 4a may eliminate one spherical rank entirely in the special circumstance where β is set to the magic angle of that rank[29]. The magic angle $\beta^{(l)}$ for rank l is defined by $d_{00}^l(\beta^{(l)}) = P_l(\cos \beta^{(l)}) = 0$, and the first few values are $\beta^{(\text{odd})} = \pi/2$, $\beta^{(2)} = \arccos(1/\sqrt{3}) \approx 54.736^\circ$.

An extension of this concept is to chain several magic-angle filters together, so that the successive elimination of ranks approximates to a single-scan filter for scalar spin order. The sequence shown in Figure 4(b) is composed of two filters, the first one using a magic angle $\beta^{(\text{odd})} = \pi/2$ and the second using $\beta^{(2)} = \arccos(1/\sqrt{3}) \approx 54.7^\circ$ having the overall effect of dephasing the spin ranks 1, 2 and 3. These chained filters are successful provided that there is no inter-rank conversion of spin order during the delay time between the RF

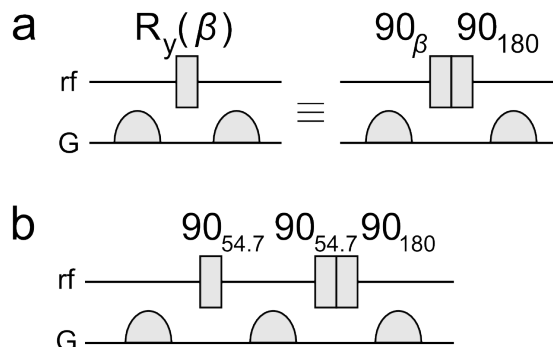


Figure 4: Filters involving field gradient (G) and radiofrequency (rf) pulses: (a) basic element; (b) single-scan filter to dephase spin order of rank $0 < l \leq 3$.

pulses. Transfer of spin order between ranks can arise if the spin system contains two or more magnetically inequivalent nuclei and the inter-pulse duration is of comparable magnitude to the inverse of the spin-spin scalar coupling strengths. In systems with magnetic equivalence (e.g. H_2 , CH_3X) or nearly magnetically equivalent systems (e.g. chemically inequivalent spin pairs in the strong coupling limit[12, 30, 31]) conversion between spin ranks is very slow, or even forbidden, and this filtering method is a popular option.

3.3 Other methods

The pulsed-field-gradient methods described in Section 3.2.2 dephase only spin coherences ($|m| > 0$) and not populations ($m = 0$). As a more general approach to the single-scan filter concept, one can consider truly “brute force” approaches in which all spin order with $l \geq 1$ is dephased simultaneously.

One method is to irradiate the spin system with a resonant, spatially inhomogeneous rf magnetic field in addition to the main static field of the NMR apparatus[15]. In the resonant frame of the nuclei, the effective nutation axis may approximate a near-uniform distribution across the sample and therefore near uniform sampling of the rotation group (Equation 25). Phase modulation of the irradiation (e.g. WALTZ-16) increases the effectiveness further[32].

Instead of reorienting the axis of effective field in the resonant rotating frame of the nuclei, the same averaging effect can be generated by non-adiabatic switching of the magnetic field orientation in the laboratory frame. This approach cannot be implemented if the main field of the NMR instrument is provided by persistent magnets (superconducting magnets, rare-earth magnets), but is an option for low-field NMR if hardware allows the orientation of magnetic field to be changed arbitrarily (e.g. triple coils). At very low magnetic fields in the microtesla range, random reorientations of the effective field can also occur when the sample is mechanically vibrated or shaken by hand in a field gradient. Sufficiently strong gradients can be generated near the surfaces of a Mu-metal shielding cans in the earth’s magnetic field[33].

Finally, there is one caveat to seeking filters for scalar spin order as an approximation for long-lived spin order. While long-lived spin order is almost always scalar order, the reverse statement must be considered: not all scalar order is long lived. The only method guaranteed to eliminate short-lived components of the NMR signal is a “relaxation filter” where a time delay τ_{relax} introduced to attenuate unwanted spin order by decoherence[34]. Assuming decoherence times for long-lived spin order T_{LLS} and other spin order $T' < T_{\text{LLS}}$ the fidelity of such a filter can be defined as $1 - \exp[-\tau_{\text{relax}}/(1/T' - 1/T_{\text{LLS}})]$. The success of this simple approach therefore depends on the contrast between relaxation times.

4 Applications

4.1 Hyperpolarized long-lived states

Scalar spin order is central to the phenomenon of quantum-rotor-induced polarization (QRIP). QRIP occurs in molecules where two or more spin-1/2 nuclei have an intrinsic magnetic equivalence and the quantized nuclear-spin and rotational angular momentum states are represented by the same symmetry group. The Pauli exclusion principle only permits overall antisymmetric product states of rotation and nuclear spin angular momenta with respect to pairwise exchange of equivalent spin-1/2 nuclei. Consequently, scalar spin order may be populated at the thermal equilibrium even in the absence of magnetic fields. Furthermore if the scalar order is long-lived due to relaxation processes being symmetry forbidden, the amplitude of scalar order can be greatly enhanced at room temperature after transient cooling of the system to below the characteristic rotational temperature (θ_{rot}) in the presence of a paramagnetic catalyst.

The hydrogen diatomic (H_2 , $\theta_{\text{rot}} = 87.6$ K) has the smallest moment of inertia of any quantum rotor with nuclear magnetic equivalence and consequently demonstrates the strongest QRIP effect. The singlet or ‘para’ nuclear spin isomer $|S_0\rangle$ is paired with even values of the rotational quantum number $J = 0, 2, 4, \dots$ and the triplet $|T_m\rangle$ is paired with odd values $J = 1, 3, \dots$ resulting in a non-zero population of scalar spin order given by

$$\text{Tr}(Q_{\text{LLS}}^{\text{ST}\dagger}\rho) = \frac{\sum_{J=0}^{\infty} (-1)^J (2J+1)^2 e^{-\theta_{\text{rot}} J(J+1)/T}}{\sum_{J=0}^{\infty} (2J+1)^2 e^{-\theta_{\text{rot}} J(J+1)/T}}. \quad (31)$$

At 77 K the scalar order (or para-hydrogen) fraction corresponds to a $\sim 50\%$ overall polarization of the spin system and at 20 K the value rises to $\sim 90\%$. Small molecules with rapid internal rotation of methyl groups are also known to exhibit hyperpolarized long-lived spin order produced by the QRIP mechanism, of the type $Q_{\text{LLS}}^{\text{AE}}$ (Equation 19). These include acetonitrile, acetate, picoline and xylene. The phenomenon is historically known as the Haupt effect [35].

In particular, the hyperpolarized long-lived spin order of para-hydrogen (H_2 populated in the nuclear singlet state) can be exploited by a number of chemical procedures generally termed para-hydrogen induced polarization (PHIP) to furnish hyperpolarized nuclear spin order in ordinary molecules, which may

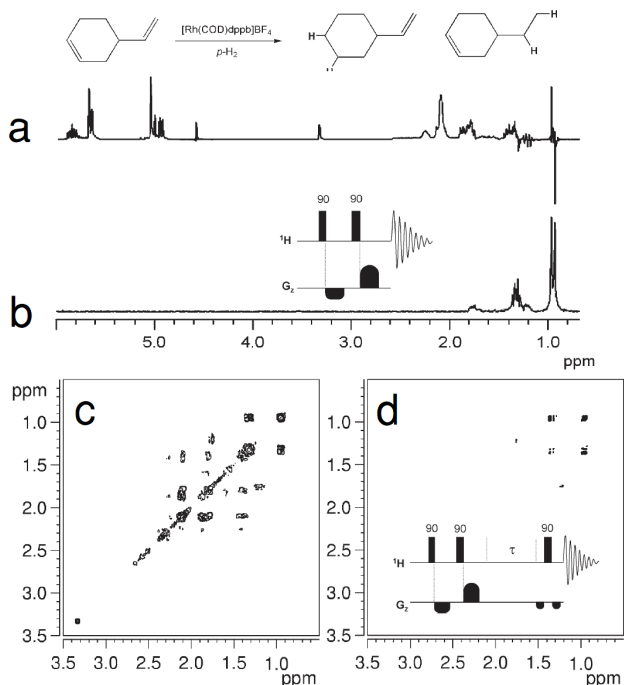


Figure 5: [Figure reproduced from Royal Society of Chemistry publication DOI:10.1039/B616307F] = Ref [39]. Scalar-spin-order filtering in only-para-hydrogen spectroscopy (OPSY): (a) para-hydrogen-enhanced ^1H NMR spectrum of a sample containing 4-vinylcyclohexene (10 μL , 3 bar para- H_2); (b) ^1H OPSY spectrum; (c) para- H_2 ^1H - ^1H correlation spectroscopy (COSY); (d) OPSY-filtered COSY.

also be long lived[31, 36, 37, 38]. The procedure of filtering of PHIP signals has acquired the name ‘only-para-hydrogen spectroscopy’ (OPSY).[39, 40, 41] A scalar order filter is used to ensure that only the hyperpolarized spin species produce visible signals in the NMR spectrum and not spin order from other species in the sample, e.g. the solvent. The effect is illustrated by the contrasting pulse-acquire spectra in Figures 5a and 5b, as well as the two-dimensional correlation spectra in Figures 5c and 5d. The most frequently used OPSY techniques involve the magic-angle filters described in Section 3.2.3, and often only a single $\beta^{(\text{odd})} = \pi/2$ pulse is used.

4.2 Magnetization-to-scalar-order conversion

There now exists a collection of radiofrequency pulse sequences whose task is to populate scalar spin order starting from the equilibrium Zeeman polarization in an NMR spin system[2, 26, 42, 43, 44]. To achieve maximum conversion efficiency, many of the pulse sequence parameters (e.g. time delays) must be

tailored to the resonance frequencies of the spin system. If the frequencies are unknown, or there are errors to consider, then these can be measured indirectly through the amplitude of target spin order generated. An initial state of magnetization is converted to scalar order, filtered, then immediately converted back to be detected in the form of magnetization by applying the first pulse sequence in reverse chronological order. The filter ensures that the amplitude of the observed signal is proportional to the conversion efficiency. Filtering may also be useful in molecules that support multiple functional groups with scalar spin order. As an illustrative example, the molecule strychnine can be prepared with scalar spin order populated on four of its CH_2 groups as shown in Figure 6.

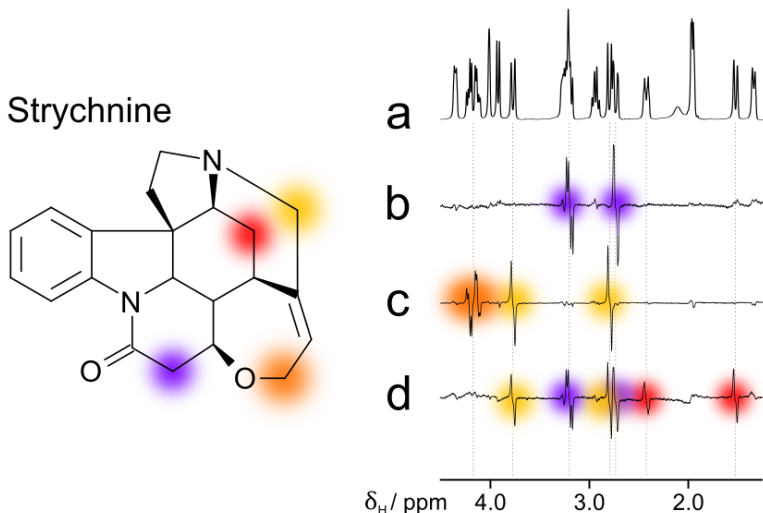


Figure 6: [Unpublished work by the author] ^1H NMR of 10 mg strychnine in chloroform- d : (a) single scan pulse-acquire spectrum; (b-d) anti-phase signals arising from scalar spin order on the diastereotopic CH_2 groups, highlighted in color, detected using the same pulse sequence as Figure 3b(ii), various delay times, and using a tetrahedral filter.

The rotational invariance of scalar spin order is also a desirable property for NMR quantum information processing, since scalar spin order emulates the behavior of a pure state[45]. Initialization procedures in experimental NMR quantum computing may involve applying magnetization-to-scalar pulse sequences to the spin system’s thermal equilibrium Zeeman spin polarization, or PHIP, followed by a scalar order filter[46, 47, 48].

4.3 Relaxation measurements

It can be proved that conversion between thermally populated Zeeman order and singlet-triplet population difference order $|Q_{\text{LLS}}^{\text{ST}}|$ cannot exceed $\sqrt{2/3} \approx 82\%$ efficiency[49]. Therefore most magnetization-to-singlet converting pulse

sequences result in spin order by-products of spherical rank $l > 0$ even under the best experimental conditions. These additional terms may obscure the exponential decay curves from which relaxation rates of the long-lived spin order may be fitted, especially when lifetimes of scalar order are close in magnitude to T_1 and T_2 . For accurate measurement of the relaxation times, signals from the by-product spin order should be removed by filtering, see Figure 7.

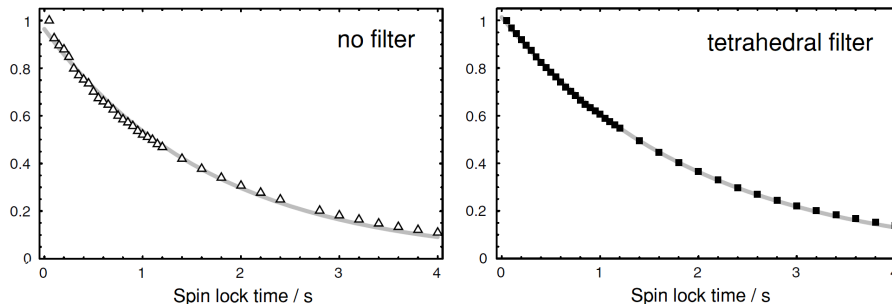


Figure 7: [Figure reproduced from publication DOI:10.1016/j.jmr.2007.11.021] = Ref. [25]. Re-use permission granted by Elsevier. Experimental decay of the long-lived ^1H singlet-triplet population difference in citric acid ($[\text{CH}_2\text{COOH}]_2\text{COHCOOH}$) as a function of spin lock interval, with and without isotropic filtering. The best-fit single-exponential decay curves (shown by gray lines) are obtained using the 12-scan tetrahedral filter.

5 Conclusions

In this chapter, methods have been presented for ‘filtering’ spin order that corresponds to a totally symmetric representation of the molecular symmetry group – a property that is generally identified with, but not limited to, decoherence-free nuclear spin order. These filters share a common principle of rotation quadrature in three-dimensional space that may easily be implemented on an NMR spectrometer with radiofrequency pulse capabilities, and if necessary may further be combined with conventional phase cycling methods that select the NMR signals of interest based on their coherence transfer pathway [50, 51]. With the present growth in exploitation of long-lived spin order across NMR, the future may expect to see scalar-order filters become a more standard experimental practice.

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