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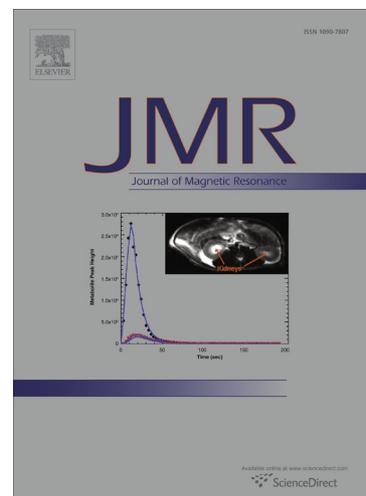Please cite this article as: M.H. Levitt, Symmetry Constraints on Spin Dynamics: Application to Hyperpolarized NMR, *Journal of Magnetic Resonance* (2015), doi: http://dx.doi.org/10.1016/j.jmr.2015.08.021

Symmetry Constraints on Spin Dynamics: Application to Hyperpolarized NMR

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Abstract

Spin dynamical evolution is constrained by the symmetries of the spin Hamiltonians that generate the quantum dynamics. The consequences of symmetry-induced constraints are examined for some common hyperpolarized NMR experiments, including the excitation of singlet order in spin-pair systems, and the transfer of parahydrogen-induced hyperpolarized singlet order to magnetization in systems displaying chemical and magnetic equivalence.

Keywords: unitary bounds, spin dynamics, permutation symmetry, magnetic equivalence, chemical equivalence, long-lived states

1. Introduction

There are fundamental bounds on the coherent transformations of spin density operator components, associated with the conservation of eigenvalues under unitary transformation [1, 2, 3, 4]. If the eigenvalue spectra of the two operators match, a complete transformation of one operator component into another is possible. In the general case, however, the two operators have different sets of eigenvalues, so that a complete transformation of one into the other is physically impossible. In a series of papers, Sørensen and co-workers defined the limiting value of the transformation amplitude for one density operator component into another. These results were applied to a variety of NMR problems, including polarization transfer between spin species [1, 2, 3, 4, 5, 6], and cross-polarization in solids [7, 8, 6]. Extensions to non-Hermitian operators and non-unitary dissipative evolution were developed [9, 10, 11].

In their original version, the Sørensen bounds did not take into account the selection rules associated with the symmetries of the spin Hamiltonian which drive the transformation. It was later shown that permutation symmetries for the spin Hamiltonians, associated with magnetic equivalence, lead to additional restrictions [6, 12]. These results were applied to problems of polarization transfer in weakly-coupled spin systems of the type $A_N X$, where $N = 1, 2, 3 \ldots$. In such systems, the maximum possible transformation of a single component of net angular momentum from the A-spins to the X-spins is not influenced by magnetic equivalence of the A-spins [6, 12]. On the other hand, magnetic equivalence does constrain the simultaneous transfer of two Cartesian components of angular momentum, as described by the transformations of non-Hermitian operators of the type I^- [12].

In this article, the topic of symmetry-constrained bounds on spin dynamics is revisited, in the context of recent hyperpolarized NMR experiments. I examine closely the spin dynamical manipulations of four-spin systems, involving long-lived spin states [13, 14, 15, 16, 17] and SABRE (Signal Amplification by Reversible Exchange) experiments [18, 19, 20, 21, 22]. Such experiments sometimes involve four-spin-1/2 systems of the type $A_2 X_2$ (two magnetically equivalent pairs) or $AA'XX'$ (two chemically equivalent but magnetically inequivalent pairs). How does the chemical or magnetic equivalence of the spin systems restrict the possible transformations of the density operator in such systems?

The following simple example motivates this investigation. Consider a spin system comprising two

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spins-1/2 of species I and two spins-1/2 of species S. Label the spins I_1, I_2, S_3 and S_4. The J-couplings are denoted J_{12}, etc. If the I-spins are chemically equivalent, and similarly for the S-spins, the spin system may be of type A_2X_2 or $AA'XX'$, depending on the network of spin-spin couplings. If all four I-S couplings are the same ($J_{13} = J_{14} = J_{23} = J_{24}$), the I and S-spins are magnetically equivalent, so the system is of type A_2X_2. If, on the other hand, the spin-spin couplings are found in symmetrical pairs ($J_{13} = J_{24} \neq J_{14} = J_{23}$), the I-spins are chemically equivalent but magnetically inequivalent, and similarly for the S-spins. The spin system is denoted $AA'XX'$ in this case.

Consider the transformation of total I-spin polarization into total S-spin polarization, described by

$$UI_zU^{\dagger} = bS_z + C \qquad (1)$$

where $I_z = I_{1z} + I_{2z}$, $S_z = S_{3z} + S_{4z}$, U is a unitary operator ($U^{\dagger} = U^{-1}$), and the operator C is orthogonal to S_z, i.e. $\text{Tr}\{S_z^{\dagger}C\} = 0$. What is the maximum possible value of the coefficient b, for any unitary transformation?

Since the operators I_z and S_z have the same set of eigenvalues, a complete transformation of I_z into S_z certainly appears possible, i.e. $b_{\max} = 1$. This result is indeed correct for the case of magnetic inequivalence ($AA'XX'$) or lower symmetry. However, as shown below, the complete transformation of I_z into S_z cannot be attained for the case of magnetic equivalence (A_2X_2). The maximum transformation amplitude is only 0.75 in this case. Any attempt to convert the operator component I_z completely into the operator S_z by a unitary transformation is doomed to failure for a magnetically equivalent system of the A_2X_2 type. To my knowledge, this particular case was not described before.

This example shows that magnetic equivalence may impose non-intuitive bounds on the transformations of the spin density operator. As discussed below, such symmetry-imposed bounds are relevant to several experiments of current interest, such as SABRE [18, 19, 20, 21, 22].

To facilitate discussion of this topic, the theory of unitary bounds in the presence of symmetry, as developed by Sørensen and co-workers [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12] is reviewed and reformulated with a revised notation, and combined with a more detailed discussion of spin permutation symmetry.

2. Unitary Bounds

Consider the transformation of a density operator component A into a different operator component B by a unitary transformation, as follows:

$$UAU^{\dagger} = bB + C \qquad (2)$$

where $U^{\dagger} = U^{-1}$, and the operator C is orthogonal to B:

$$\text{Tr}\{B^{\dagger}C\} = 0 \qquad (3)$$

The transformation amplitude b is bounded as follows [1, 2, 3, 4]:

$$b_{\min} \leq b \leq b_{\max} \qquad (4)$$

where

$$\begin{aligned} b_{\min} &= \|B\|^{-2} \, \Lambda_A{\uparrow} \cdot \Lambda_B{\downarrow} \\ b_{\max} &= \|B\|^{-2} \, \Lambda_A{\uparrow} \cdot \Lambda_B{\uparrow} \end{aligned} \qquad (5)$$

and the norm-squared of operator B is given by

$$\|B\|^2 = \Lambda_B{\uparrow} \cdot \Lambda_B{\uparrow} \qquad (6)$$

Here $\Lambda_A{\uparrow}$ and $\Lambda_A{\downarrow}$ are vectors containing the eigenvalues of the operator A, arranged in ascending and descending order respectively, and similarly for $\Lambda_B{\uparrow}$ and $\Lambda_B{\downarrow}$. If the operators A and B have the same eigenvalue spectrum, complete transformation of A into B is theoretically possible by unitary transformation ($b_{\max} = 1$). In other cases, the limits on the transformation of A into B are set by equations 5.

3. Spin Permutations

3.1. Spin Permutation Operators

Consider an ensemble composed of isolated spin systems of N coupled spins-1/2. The quantum state of one spin system is a superposition of the 2^N Zeeman product states, denoted $|\alpha_1\beta_2 \ldots \alpha_N>$, where the symbols $\{\alpha_j, \beta_j\}$ denote states with angular momentum of spin I_j given by $\pm\frac{1}{2}\hbar$ along the main magnetic field.

A spin permutation operation denoted (jk) [23, 24] exchanges the states of spins j and k, for example:

$$(12)|\alpha_1\beta_2> = |\beta_1\alpha_2> \qquad (7)$$

Permutations may be multiplied, for example:

$$(12)(34)|\alpha_1\beta_2\beta_3\alpha_4> = |\beta_1\alpha_2\alpha_3\beta_4> \qquad (8)$$

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The identity operator (null permutation) is denoted here by empty brackets ():

$$()|\alpha_1\beta_2> = |\alpha_1\beta_2> \qquad (9)$$

Permutations involving shared spins in consecutive operations may be condensed, for example:

$$(123) = (12)(23) \qquad (10)$$

The notation (123) indicates the cyclic permutation $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$, etc.

Sandwiching a spin operator with the permutation operators exchanges the spin indices, for example:

$$(12)I_{1z}(12)^{\dagger} = I_{2z} \qquad (11)$$

where $(jk) = (jk)^{\dagger} = (jk)^{-1}$.

3.2. Spin Permutation Groups

A group of spin permutations, denoted $\mathcal{G}$, is a set of spin permutation operations that satisfies the standard group conditions (all products of group members, the inverse of each group member, and the identity operator, are all in the same set) [23, 24].

An irreducible representation (irrep) Γ of a group $\mathcal{G}$ is spanned by a minimal set of spin states $\mathcal{S}^{\Gamma}$ such that any element of $\mathcal{G}$, applied to a state in the set, leads to a superposition of spin states in the same set:

$$P|r> = \sum_{|s> \in \mathcal{S}^{\Gamma}} P_{sr}|s> \qquad (12)$$

where $P \in \mathcal{G}$ and $|r> \in \mathcal{S}^{\Gamma}$. A given irrep Γ is defined by the set of characters χ^{Γ} for the permutation elements P, where

$$\chi^{\Gamma}(P) = \sum_{|s> \in \mathcal{S}^{\Gamma}} P_{ss} \qquad (13)$$

The characters of the irreps for common groups are listed in the standard texts [23, 24].

3.2.1. Two spins-1/2

In the case of two spins, the following two permutations form a group:

$$\mathcal{G}^{12} = \{(),(12)\} \qquad (14)$$

The group $\mathcal{G}^{12}$ has two irreps, denoted here g and u, where the symbols g and u indicate "even" (*gerade*) and "odd" (*ungerade*) in German. These have characters $\chi_g^{12}() = \chi_u^{12}() = 1$ and $\chi_g^{12}(12) = +1$

and $\chi_u^{12}(12) = -1$, indicating sets of states with even and odd parity with respect to spin exchange.

The u irrep is spanned by an isolated state:

$$\mathcal{S}_u^{12} = \{|S_0^{12}>\} \qquad (15)$$

where the singlet state is given by:

$$|S_0^{12}> = 2^{-1/2}\left(|\alpha_1\beta_2> - |\beta_1\alpha_2>\right) \qquad (16)$$

The g irrep is spanned by the three triplet states:

$$\mathcal{S}_g^{12} = \{|T_{+1}^{12}>, |T_0^{12}>, |T_{-1}^{12}>\} \qquad (17)$$

where

$$
\begin{aligned}
|T_{+1}^{12}> &= |\alpha_1\alpha_2> \\
|T_0^{12}> &= 2^{-1/2}\left(|\alpha_1\beta_2> + |\beta_1\alpha_2>\right) \\
|T_{-1}^{12}> &= |\beta_1\beta_2>
\end{aligned}
\qquad (18)
$$

3.2.2. Four spins-1/2: Magnetic equivalence group

In the case of four spins, many permutation groups may be constructed. In this article we only consider groups involving the pair exchanges (12) and (34), excluding exchanges of the type (13), (14), (23) and (24). These groups will be sufficient for discussing the cases of magnetic and chemical equivalence in four-spin systems.

The *magnetic equivalence group* is formed from the direct products of the permutation groups for the spin pairs $\{1,2\}$ and $\{3,4\}$:

$$\mathcal{G}_{\mathrm{ME}}^{12,34} = \mathcal{G}^{12} \otimes \mathcal{G}^{34} = \{(),(12),(34),(12)(34)\} \quad (19)$$

The magnetic equivalence group $\mathcal{G}_{\mathrm{ME}}^{12,34}$ has four irreps which are denoted here gg, uu, gu and ug. The irreps uu and ug are spanned by states that change sign upon exchange of spins I_1 and I_2, while the irreps uu and gu are spanned by states that change sign upon exchange of spins S_3 and S_4. States in the irrep gg are invariant to both spin exchanges.

The irreps of the magnetic equivalence group are spanned by direct products of the singlet and triplet states, as follows:

$$
\begin{aligned}
\mathcal{S}_{gg}^{12,34} &= \mathcal{S}_g^{12} \otimes \mathcal{S}_g^{34} \\
\mathcal{S}_{uu}^{12,34} &= \mathcal{S}_u^{12} \otimes \mathcal{S}_u^{34} \\
\mathcal{S}_{gu}^{12,34} &= \mathcal{S}_g^{12} \otimes \mathcal{S}_u^{34} \\
\mathcal{S}_{ug}^{12,34} &= \mathcal{S}_u^{12} \otimes \mathcal{S}_g^{34}
\end{aligned}
\qquad (20)
$$

For example the irrep gg is spanned by 9 triplet-triplet product states, of the form $|T_M^{12}T_{M'}^{23}>$, where $M, M' \in \{+1, 0, -1\}$. The irrep uu is spanned by

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the singlet-singlet product state $|S_0^{12} S_0^{23}>$. The irrep gu is spanned by 3 states of the form $|T_M^{12} S_0^{23}>$, while the irrep ug is spanned by 3 states of the form $|S_0^{12} T_M^{23}>$. The total dimension $9+1+3+3 = 16 = 2^4$ is equal to the number of states for four spins-$1/2$.

The singlet-triplet product basis (equation 20) has been used extensively for the study of long-lived states and SABRE phenomena [14, 15, 16, 17, 21, 22].

3.2.3. Four spins-1/2: Magnetic inequivalence group

The *magnetic inequivalence group* for four spins-$\frac{1}{2}$ is composed of only the null permutation and the double permutation:

$$\mathcal{G}_{\mathrm{MIE}}^{12,34} = \{(), (12)(34)\} \qquad (21)$$

The group $\mathcal{G}_{\mathrm{MIE}}^{12,34}$ has only two irreps, denoted g and u, which are sums of irreps for the magnetic equivalence case:

$$
\begin{aligned}
\mathcal{S}_g^{12,34} &= \mathcal{S}_{gg}^{12,34} \oplus \mathcal{S}_{uu}^{12,34} \\
\mathcal{S}_u^{12,34} &= \mathcal{S}_{gu}^{12,34} \oplus \mathcal{S}_{ug}^{12,34}
\end{aligned} \qquad (22)
$$

For the 4-spin-1/2 system, the g irrep is spanned by 10 states (nine triplet-triplet states, and one singlet-singlet state), while the u irrep is spanned by 6 states (three triplet-singlet states, and three singlet-triplet states).

4. Symmetry Constraints on Spin Dynamics

4.1. Symmetrical operators

Consider an operator Q which commutes with all elements of a permutation group $\mathcal{G}$, i.e.

$$PQ = QP \ ; \qquad \forall P \in \mathcal{G} \qquad (23)$$

This is called a *symmetric operator* under the group $\mathcal{G}$. From the vanishing-integral rule [23, 24], a symmetrical operator has a block-diagonal matrix representation in the basis of states that span the irreps of $\mathcal{G}$, i.e.

$$<r|Q|s> = 0 \text{ if } |r> \in \mathcal{S}^\Gamma, |s> \in \mathcal{S}^{\Gamma'} \text{ and } \Gamma \neq \Gamma' \qquad (24)$$

It follows that the symmetrical operator Q may be decomposed into components each transforming under a different irrep of the group $\mathcal{G}$:

$$Q = \sum_\Gamma Q^\Gamma \qquad (25)$$

where the component Q^Γ is given by

$$Q^\Gamma = \sum_{\{r,s\} \in \mathcal{S}^\Gamma} <r|Q|s> |r><s| \qquad (26)$$

Each irreducible component Q^Γ has a set of eigenvalues, denoted Λ_Q^Γ. The complete set of eigenvalues is the collation of these subsets:

$$\Lambda_Q = \Lambda_Q^{\Gamma_1} \oplus \Lambda_Q^{\Gamma_2} \oplus \ldots \qquad (27)$$

The symmetry-constrained bounds involve sorting of the eigenvalue sets, either in ascending or descending order. The symbol $\Lambda_Q^\Gamma \uparrow$ denotes the eigenvalues of that block in the matrix representation of Q which transforms according to the irrep Γ, sorted in ascending order. The symbol $\Lambda_Q^\Gamma \downarrow$ denotes sorting of eigenvalues in descending order. When the eigenvalues from different irreps are collated to construct the total eigenvalue sets $\Lambda_Q \uparrow$ and $\Lambda_Q \downarrow$, the sorting usually reshuffles eigenvalues belonging to different irreps.

4.2. Evolution under symmetrical Hamiltonians

Suppose that spin evolution occurs under a Hamiltonian operator $\mathcal{H}$, which is symmetric under the permutation group $\mathcal{G}$. The unitary evolution operator $U(t, t_0)$ from the initial time point t_0 to a general time t solves the Liouville von-Neumann equation:

$$\frac{d}{dt} U(t, t_0) = -i\mathcal{H}(t) U(t, t_0) \qquad (28)$$

with the initial condition $U(t_0, t_0) = 1$. If the Hamiltonian $\mathcal{H}$ is symmetrical under the permutation group $\mathcal{G}$, the unitary evolution operator factorises into separate evolution operators for the irreps of $\mathcal{G}$:

$$U = U^\Gamma U^{\Gamma'} \ldots \qquad (29)$$

where

$$\frac{d}{dt} U^\Gamma(t, t_0) = -i\mathcal{H}^\Gamma(t) U^\Gamma(t, t_0) \qquad (30)$$

The evolution operator for an irrep Γ commutes with operators transforming according to a different irrep Γ':

$$U^\Gamma Q^{\Gamma'} U^{\Gamma\dagger} = Q^{\Gamma'} \ ; \qquad \Gamma \neq \Gamma' \qquad (31)$$

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4.3. Symmetry-constrained bounds

Consider the transformation in eq. 2, in the case that both operators A and B, as well as the Hamiltonian $\mathcal{H}$ generating the evolution, are all symmetric under the group $\mathcal{G}$.

The initial operator A and target operator B may be written in terms of their irreducible components:

$$A = \sum_{\Gamma} A^{\Gamma}$$

$$B = \sum_{\Gamma} B^{\Gamma} \tag{32}$$

The transformation of A into B involves simultaneous transformations of all the irreducible components:

$$U^{\Gamma} A^{\Gamma} U^{\Gamma\dagger} = b^{\Gamma} B^{\Gamma} + C^{\Gamma} \tag{33}$$

where $\mathrm{Tr}\{B^{\Gamma\dagger} C^{\Gamma}\} = 0$. The transformation coefficients are subject to the unitary bounds (equation 5):

$$b_{\min}^{\Gamma} \le b^{\Gamma} \le b_{\max}^{\Gamma} \tag{34}$$

where

$$\begin{aligned} b_{\min}^{\Gamma} &= \left\|B^{\Gamma}\right\|^{-2} \Lambda_A^{\Gamma}{\uparrow} \cdot \Lambda_B^{\Gamma}{\downarrow} \\ b_{\max}^{\Gamma} &= \left\|B^{\Gamma}\right\|^{-2} \Lambda_A^{\Gamma}{\uparrow} \cdot \Lambda_B^{\Gamma}{\uparrow} \end{aligned} \tag{35}$$

The maximum coefficient $b_{\max}^{\mathrm{SC}}$ for the symmetry-constrained transformation of operator A into operator B is therefore given by

$$\begin{aligned} b_{\max}^{\mathrm{SC}} &= \frac{\mathrm{Tr}\{B^{\dagger} U A U^{\dagger}\}}{\mathrm{Tr}\{B^{\dagger} B\}} \\ &= \|B\|^{-2} \sum_{\Gamma} b_{\max}^{\Gamma} \left\|B^{\Gamma}\right\|^2 \\ &= \|B\|^{-2} \sum_{\Gamma} \Lambda_A^{\Gamma}{\uparrow} \cdot \Lambda_B^{\Gamma}{\uparrow} \end{aligned} \tag{36}$$

Similarly the symmetry-constrained minimum transformation coefficient $b_{\min}^{\mathrm{SC}}$ is given by

$$b_{\min}^{\mathrm{SC}} = \|B\|^{-2} \sum_{\Gamma} \Lambda_A^{\Gamma}{\uparrow} \cdot \Lambda_B^{\Gamma}{\downarrow} \tag{37}$$

Equations 36 and 37 represent the generalisations of the unitary bounds for the case that the initial operator A, the target operator B, and the spin Hamiltonian $\mathcal{H}$, are all symmetric under a permutation group $\mathcal{G}$.

In general, the symmetry-constrained bounds either lie inside, or coincide with, the unconstrained bounds:

$$b_{\min} \le b_{\min}^{\mathrm{SC}} \le b_{\max}^{\mathrm{SC}} \le b_{\max} \tag{38}$$

The difference between the symmetry-constrained and unconstrained bounds lies in the way the operator eigenvalues are collated and sorted. In the absence of symmetry, all eigenvalues are collated and arranged in ascending order before the dot product is taken. In the symmetry-constrained bound, the eigenvalues are first grouped according to irrep and the subsequent ordering only takes place within each irrep. This subtle difference has notable consequences.

5. Examples

5.1. Spin-1/2 pairs

We examine the bounds on the transformation of the spin density operator for spin-$\frac{1}{2}$ pairs, contrasting the cases in which the spin Hamiltonian does, or does not, possess exchange symmetry.

5.1.1. Magnetization to singlet order

The transformation of total spin magnetization into singlet order, and back again, is an important manipulation in the NMR of long-lived states [13, 14, 15, 16, 17, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44] and in parahydrogen-enhanced NMR [18, 19, 20, 21, 22, 45, 46, 47, 48, 49].

The total z-angular momentum operator for the two spins is defined as follows:

$$I_z = I_{1z} + I_{2z} \tag{39}$$

Singlet order represents the difference in population between the singlet state and the mean of the triplet state populations. A suitable operator is as follows:

$$Q_{\mathrm{SO}} = |S_0^{12}\rangle\langle S_0^{12}| - \frac{1}{3} \sum_{M=-1}^{+1} |T_M^{12}\rangle\langle T_M^{12}| \tag{40}$$

which is proportional to the scalar product of the spin angular momentum operators:

$$Q_{\mathrm{SO}} = -\frac{4}{3}\mathbf{I}_1 \cdot \mathbf{I}_2 \tag{41}$$

Both operators I_z and Q_{SO} are symmetric with respect to the group $\mathcal{G}^{12}$.

The ordered eigenvalues of the two operators are as follows:

$$\Lambda_z\uparrow \;=\; \begin{pmatrix} +1 \\ 0 \\ 0 \\ -1 \end{pmatrix}$$

$$\Lambda_{\mathrm{SO}}\uparrow \;=\; \begin{pmatrix} +1 \\ -1/3 \\ -1/3 \\ -1/3 \end{pmatrix} \tag{42}$$

and hence

$$\|\Lambda_z\|^2 = \Lambda_z\uparrow \cdot \Lambda_z\uparrow \;=\; 2$$
$$\|\Lambda_{\mathrm{SO}}\|^2 = \Lambda_{\mathrm{SO}}\uparrow \cdot \Lambda_{\mathrm{SO}}\uparrow \;=\; 4/3 \tag{43}$$

Note that the two operators have a different norm.

1. Case of no symmetry. The bounds on the transformation of total z-angular momentum into singlet order are as follows:

$$b_{\min}(z \to \mathrm{SO}) \;=\; (3/4)\Lambda_z\uparrow \cdot \Lambda_{\mathrm{SO}}\downarrow \;=\; -1$$
$$b_{\max}(z \to \mathrm{SO}) \;=\; (3/4)\Lambda_z\uparrow \cdot \Lambda_{\mathrm{SO}}\uparrow \;=\; +1 \tag{44}$$

The reverse transformation exhibits different bounds, since the two operators have different norms:

$$b_{\min}(\mathrm{SO} \to z) \;=\; (1/2)\Lambda_{\mathrm{SO}}\uparrow \cdot \Lambda_z\downarrow \;=\; -2/3$$
$$b_{\max}(\mathrm{SO} \to z) \;=\; (1/2)\Lambda_{\mathrm{SO}}\uparrow \cdot \Lambda_z\uparrow \;=\; +2/3 \tag{45}$$

The optimum amplitude for passing magnetization through singlet order and back into magnetization is given by the product of the $b_{\max}$ values:

$$b_{\max}(z \to \mathrm{SO} \to z)$$
$$= b_{\max}(z \to \mathrm{SO})b_{\max}(\mathrm{SO} \to z) = 2/3 \tag{46}$$

It follows that passing spin-pair magnetization through singlet order inevitably loses $1/3$ of the magnetization (assuming that only singlet order is retained after the first transformation). In principle, existing methods such as M2S/S2M (magnetization-to-singlet) [38, 39] and SLIC (spin-lock-induced crossing) [40, 41] attain this theoretical optimum (in the absence of relaxation and other losses). The non-converted magnetization fraction is often visible as a rapidly-decaying initial component in singlet NMR experiments [32, 36, 42].

2. Case of exchange symmetry. If the Hamiltonians generating the spin evolution are symmetric under spin exchange, the feasible transformations are bounded by equations 36 and 37 for the group $\mathcal{G}^{12}$.

To evaluate these bounds, the operator eigenvalues are grouped by irrep before sorting. The eigenvalue vectors, with elements arranged in ascending order within each irrep, are as follows:

$$\Lambda_z^g\uparrow \;=\; \begin{pmatrix} +1 \\ 0 \\ -1 \end{pmatrix}$$

$$\Lambda_{\mathrm{SO}}^g\uparrow \;=\; \begin{pmatrix} -1/3 \\ -1/3 \\ -1/3 \end{pmatrix}$$

$$\Lambda_z^u\uparrow \;=\; (0)$$
$$\Lambda_{\mathrm{SO}}^u\uparrow \;=\; (1) \tag{47}$$

and hence

$$\|\Lambda_z^g\|^2 \;=\; \Lambda_z^g\uparrow \cdot \Lambda_z^g\uparrow \;=\; 2$$
$$\|\Lambda_{\mathrm{SO}}^g\|^2 \;=\; \Lambda_{\mathrm{SO}}^g\uparrow \cdot \Lambda_{\mathrm{SO}}^g\uparrow \;=\; 1/3$$
$$\|\Lambda_z^u\|^2 \;=\; \Lambda_z^u\uparrow \cdot \Lambda_z^u\uparrow \;=\; 0$$
$$\|\Lambda_{\mathrm{SO}}^u\|^2 \;=\; \Lambda_{\mathrm{SO}}^u\uparrow \cdot \Lambda_{\mathrm{SO}}^u\uparrow \;=\; 1$$

The symmetry-constrained transformation bounds are therefore given by:

$$b_{\min}^{\mathrm{SC}}(z \to \mathrm{SO}) =$$
$$(3/4)\,(\Lambda_z^g\uparrow \cdot \Lambda_{\mathrm{SO}}^g\downarrow + \Lambda_z^u\uparrow \cdot \Lambda_{\mathrm{SO}}^u\downarrow) = 0$$

$$b_{\max}^{\mathrm{SC}}(z \to \mathrm{SO}) =$$
$$(3/4)\,(\Lambda_z^g\uparrow \cdot \Lambda_{\mathrm{SO}}^g\uparrow + \Lambda_z^u\uparrow \cdot \Lambda_{\mathrm{SO}}^u\uparrow) = 0 \tag{48}$$

It follows that $b^{\mathrm{SC}}(z \to \mathrm{SO}) = 0$ for any unitary transformation. It is therefore impossible to convert total spin magnetization into singlet order by coherent means, in the case that the spin Hamiltonians driving the evolution are symmetric to exchange. The same applies to the reverse transformation.

This result is well-known. For example, in parahydrogen-enhanced NMR, the chemical equivalence of the hydrogen nuclei originating with parahydrogen must be broken in order to obtain enhanced NMR signals [18, 19, 20, 21, 22, 45, 46, 47, 48, 49]. The breaking of chemical equivalence is also necessary to access singlet order in spin-pair systems, for similar reasons.

5.1.2. Strong polarization

The use of the linear operator I_z to represent the initial density operator implies a weakly-polarized spin system, appropriate for thermally polarized

nuclear spin systems at ordinary temperatures and magnetic fields. What happens if the spin system is highly polarized? For simplicity consider the case where the initial density operator corresponds to 100% polarization of the spin pair:

$$\rho_{\mathrm{pol}} = |\alpha_1\alpha_2\rangle\langle\alpha_1\alpha_2| = \frac{1}{4} - \frac{1}{2}I_z + I_{1z}I_{2z} \quad (49)$$

with eigenvalues

$$\Lambda_{\mathrm{pol}}\uparrow = \begin{pmatrix} +1 \\ 0 \\ 0 \\ 0 \end{pmatrix} \quad (50)$$

We consider the generation of singlet order from this highly-polarised state, with and without symmetry constraints.

1. Case of no symmetry. The Sørensen bounds on the generation of singlet order from a highly polarized state are given by:

$$\begin{array}{rclll} b_{\min}(\mathrm{pol} \to \mathrm{SO}) &=& (3/4)\Lambda_{\mathrm{pol}}\uparrow \cdot \Lambda_{\mathrm{SO}}\downarrow &=& -1/4 \\ b_{\max}(\mathrm{pol} \to \mathrm{SO}) &=& (3/4)\Lambda_{\mathrm{pol}}\uparrow \cdot \Lambda_{\mathrm{SO}}\uparrow &=& +3/4 \end{array}$$
$$(51)$$

The minimum and maximum bounds are asymmetric in this case.

2. Case of exchange symmetry. The eigenvalue vectors for the irreducible components of the highly polarized state are as follows:

$$\begin{array}{rcl} \Lambda_{\mathrm{pol}}^g\uparrow &=& \begin{pmatrix} +1 \\ 0 \\ 0 \end{pmatrix} \\ \Lambda_{\mathrm{pol}}^u\uparrow &=& (0) \end{array} \quad (52)$$

The symmetry-constrained bounds for the transformation of the highly polarized state into singlet order are therefore given by:

$$b_{\min}^{\mathrm{SC}}(\mathrm{pol} \to \mathrm{SO}) =$$
$$(3/4)\left(\Lambda_{\mathrm{pol}}^g\uparrow \cdot \Lambda_{\mathrm{SO}}^g\downarrow + \Lambda_{\mathrm{pol}}^u\uparrow \cdot \Lambda_{\mathrm{SO}}^u\downarrow\right) = -1/4$$

$$b_{\max}^{\mathrm{SC}}(\mathrm{pol} \to \mathrm{SO}) =$$
$$(3/4)\left(\Lambda_{\mathrm{pol}}^g\uparrow \cdot \Lambda_{\mathrm{SO}}^g\uparrow + \Lambda_{\mathrm{pol}}^u\uparrow \cdot \Lambda_{\mathrm{SO}}^u\uparrow\right) = -1/4 \quad (53)$$

Unlike the weakly-polarized state represented by the operator I_z, the highly polarized state *already contains* singlet order (with a negative sign). This is because the population in the highly-polarized state is concentrated in one of the triplet states,

implying a depletion of singlet population relative to the mean triplet population. The direct generation of singlet order by nuclear polarization has been demonstrated experimentally [33, 43, 44].

Equation 53 shows that directly-polarized singlet order cannot be changed by any further coherent transformations, unless exchange symmetry is broken.

5.2. Four spins-1/2

We now return to the four-spin system mentioned in the introduction: two chemically-equivalent spins-$\frac{1}{2}$ I_1 and I_2, and two chemically-equivalent spins-$\frac{1}{2}$ of a different species S_1 and S_2. The spins are coupled by a set of pairwise J-couplings. The spin Hamiltonian is given by

$$\mathcal{H}(t) = \mathcal{H}_{\mathrm{ext}}(t) + \mathcal{H}^0 \quad (54)$$

where $\mathcal{H}_{\mathrm{ext}}(t)$ describes the interaction with external fields, and the internal spin Hamiltonian has the following form:

$$\mathcal{H}^0 = \mathcal{H}_I + \mathcal{H}_S + \mathcal{H}_{II} + \mathcal{H}_{IS} + \mathcal{H}_{SS} \quad (55)$$

The chemical shift terms, in the rotating frame, are as follows:

$$\begin{array}{rcl} \mathcal{H}_I &=& \Omega_I(I_{1z} + I_{2z}) \\ \mathcal{H}_S &=& \Omega_S(S_{3z} + S_{4z}) \end{array} \quad (56)$$

The homonuclear J-couplings are as follows:

$$\begin{array}{rcl} \mathcal{H}_{II} &=& 2\pi J_{12}\mathbf{I}_1 \cdot \mathbf{I}_2 \\ \mathcal{H}_{SS} &=& 2\pi J_{34}\mathbf{S}_3 \cdot \mathbf{S}_4 \end{array} \quad (57)$$

The heteronuclear coupling terms have the following form:

$$\mathcal{H}_{IS} = 2\pi J_{13}I_{1z}S_{3z} + 2\pi J_{14}I_{1z}S_{4z}$$
$$+ 2\pi J_{23}I_{2z}S_{3z} + 2\pi J_{24}I_{2z}S_{4z} \quad (58)$$

In most cases, the external Hamiltonian $\mathcal{H}_{\mathrm{ext}}(t)$ commutes with all permutations of like spins, since applied magnetic fields interact identically with all spins of the same isotopic type. In chemically equivalent systems, the chemical shift interaction operators $\mathcal{H}_I$ and $\mathcal{H}_S$, as described by equation 56, also commute with all like-spin permutations. The appropriate symmetry group therefore depends on the relationships between the J-couplings:

Magnetic Equivalence. If the heteronuclear J-couplings are all equal ($J_{13} = J_{14} = J_{23} = J_{24}$),

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the pairs of I-spins and S-spins are magnetically equivalent. The internal Hamiltonian $\mathcal{H}^0$ commutes with all members of the magnetic equivalence group $\mathcal{G}_{\mathrm{ME}}^{12,34}$ (equation 19).

Magnetic Inequivalence. If only corresponding pairs of heteronuclear J-couplings are equal ($J_{13} = J_{24} \neq J_{23} = J_{14}$), the pairs of I-spins and S-spins are chemically equivalent but magnetically inequivalent. The magnetic inequivalence group $\mathcal{G}_{\mathrm{MIE}}^{12,34}$ is appropriate in this case (equation 21).

5.2.1. Polarization transfer

Consider the transformation of I-spin angular momentum I_z into S-spin angular momentum S_z by a unitary transformation. The role of symmetry in setting bounds on this process may now be addressed.

Magnetic Equivalence. Since the three operators I_z, S_z and $\mathcal{H}$ commute with all members of the group $\mathcal{G}_{\mathrm{ME}}^{12,34}$, the symmetry-constrained bounds in equations 36 and 37 apply.

The eigenvalues of the operators I_z and S_z, grouped according to the irreps of $\mathcal{G}_{\mathrm{ME}}^{12,34}$, and sorted individually, are as follows:

$$
\Lambda_{I_z}^{gg}\uparrow \;=\; \begin{pmatrix} +1 \\ +1 \\ +1 \\ 0 \\ 0 \\ 0 \\ -1 \\ -1 \\ -1 \end{pmatrix} \;=\; \Lambda_{S_z}^{gg}\uparrow
$$

$$
\Lambda_{I_z}^{uu}\uparrow \;=\; \begin{pmatrix} 0 \end{pmatrix} \;=\; \Lambda_{S_z}^{uu}\uparrow
$$

$$
\Lambda_{I_z}^{gu}\uparrow \;=\; \begin{pmatrix} +1 \\ 0 \\ -1 \end{pmatrix} \;=\; \Lambda_{S_z}^{ug}\uparrow
$$

$$
\Lambda_{I_z}^{ug}\uparrow \;=\; \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \;=\; \Lambda_{S_z}^{gu}\uparrow
$$

(59)

Note the exchange of the gu and ug eigenvalue sets for the two operators.

The norm-squared of the operator S_z is given by

$$
\|S_z\|^2 = \Lambda_{S_z}\uparrow \cdot \Lambda_{S_z}\uparrow = 8 \tag{60}
$$

The symmetry-constrained maximum bounds on the transformation of I_z into S_z, in the case of mag-

netic equivalence, is therefore given by:

$$
b_{\max}^{\mathrm{ME}}(I_z \to S_z) = \sum_{\Gamma=\{gg,uu,gu,ug\}} (1/8)\Lambda_{I_z}^{\Gamma}\uparrow \cdot \Lambda_{S_z}^{\Gamma}\uparrow = 3/4 \tag{61}
$$

The minimum bound has the opposite sign:

$$
b_{\min}^{\mathrm{ME}}(I_z \to S_z) = -3/4 \tag{62}
$$

This shows that it is physically impossible to convert all I-spin magnetization to S-spin magnetization in a magnetically equivalent system of the type A_2X_2. The best one can do is to transfer 75% of the magnetization.

Magnetic inequivalence. In the case of magnetic inequivalence the group $\mathcal{G}_{\mathrm{MIE}}^{12,34}$ applies. The eigenvalue sets $\Lambda_{I_z}^{gg}$ and $\Lambda_{I_z}^{uu}$ are combined and resorted to obtain $\Lambda_{I_z}^{g}\uparrow$, and similarly for $\Lambda_{I_z}^{gu}$ and $\Lambda_{I_z}^{ug}$ which are combined to give $\Lambda_{I_z}^{u}\uparrow$. The results are:

$$
\Lambda_{I_z}^{g}\uparrow \;=\; \begin{pmatrix} +1 \\ +1 \\ +1 \\ 0 \\ 0 \\ 0 \\ 0 \\ -1 \\ -1 \\ -1 \end{pmatrix} \;=\; \Lambda_{S_z}^{g}\uparrow
$$

$$
\Lambda_{I_z}^{u}\uparrow \;=\; \begin{pmatrix} +1 \\ 0 \\ 0 \\ 0 \\ 0 \\ -1 \end{pmatrix} \;=\; \Lambda_{S_z}^{u}\uparrow
$$

(63)

Since the eigenvalue vectors match for both irreps, complete transformation of one operator into another is possible in the case of magnetic inequivalence (spin system of type AA′XX′):

$$
\begin{aligned}
b_{\max}^{\mathrm{MIE}}(I_z \to S_z) &= 1 \\
b_{\min}^{\mathrm{MIE}}(I_z \to S_z) &= -1
\end{aligned} \tag{64}
$$

These results illustrate how the permutation symmetry of the spin Hamiltonian constrains the achievable transformations of the spin density operator.

5.2.2. Conversion of parahydrogen singlet order to magnetization

Consider the case where pure parahydrogen is reacted with a symmetrical molecule containing two

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[13]C nuclei. The resultant 4-spin-$\frac{1}{2}$ system contains two I-spins, which may be identified as protons from the parahydrogen, and two S-spins (the ^{13}C nuclei). Is it possible to convert the parahydrogen spin order into ^{13}C magnetization? How is that process bounded by the magnetic equivalence, or inequivalence, of the reaction product? Experimental and theoretical investigations of such processes have been performed [48, 21].

The initial state of complete I-spin singlet polarization is described by the following density operator:

$$
\begin{aligned}
\rho_{\mathrm{ini}} &= |S_0^{12}\rangle\langle S_0^{12}| \otimes \mathbb{1}^{34} \\
&= |S_0^{12} S_0^{23}\rangle\langle S_0^{12} S_0^{23}| \\
&\quad + \sum_{M=-1}^{+1} |S_0^{12} T_M^{23}\rangle\langle S_0^{12} T_M^{23}|
\end{aligned} \tag{65}
$$

which may be written as follows:

$$
\rho_{\mathrm{ini}} = \frac{1}{4}\mathbb{1} - \mathbf{I}_1 \cdot \mathbf{I}_2 \tag{66}
$$

Magnetic Equivalence. The eigenvalues of the operator ρ_{ini}, grouped according to the irreps of $\mathcal{G}_{\mathrm{ME}}^{12,34}$, and sorted individually, are as follows:

$$
\begin{aligned}
\Lambda_{\mathrm{ini}}^{gg}\uparrow &= \\
\Lambda_{\mathrm{ini}}^{uu}\uparrow &= \\
\Lambda_{\mathrm{ini}}^{gu}\uparrow &= \\
\Lambda_{\mathrm{ini}}^{ug}\uparrow &=
\end{aligned}
\begin{pmatrix}
0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 1 \\ 1 \\ 1
\end{pmatrix} \tag{67}
$$

If these eigenvalue vectors are compared with those for operator S_z (equation 59), it is clear that all corresponding dot products vanish, and hence:

$$
\begin{aligned}
b_{\max}^{\mathrm{ME}}(\rho_{\mathrm{ini}} \to S_z) &= 0 \\
b_{\min}^{\mathrm{ME}}(\rho_{\mathrm{ini}} \to S_z) &= 0
\end{aligned} \tag{68}
$$

It is not possible to convert I-spin singlet order into S-spin magnetization, in the case of magnetic equivalence.

Magnetic Inequivalence. In the case of chemical equivalence but magnetic inequivalence, the eigenvalues are regrouped and sorted. The corresponding vectors are as follows:

$$
\begin{aligned}
\Lambda_{\mathrm{ini}}^{g}\uparrow &= \\
\\
\\
\\
\Lambda_{\mathrm{ini}}^{u}\uparrow &=
\end{aligned}
\begin{pmatrix}
1 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 1 \\ 1 \\ 1 \\ 0 \\ 0 \\ 0
\end{pmatrix} \tag{69}
$$

In this case the symmetry-constrained transformation limits are as follows:

$$
\begin{aligned}
b_{\max}^{\mathrm{MIE}}(\rho_{\mathrm{ini}} \to S_z) &= 1/4 \\
b_{\min}^{\mathrm{MIE}}(\rho_{\mathrm{ini}} \to S_z) &= -1/4
\end{aligned} \tag{70}
$$

The partial conversion of I-spin singlet order into S-spin magnetization in systems of the type AA′XX′ is exploited in high-field SABRE experiments [20, 21].

No symmetry. If the spin system has no symmetry (chemical inequivalence, or a non-symmetric pattern of J-couplings), the unconstrained unitary bounds apply:

$$
\begin{aligned}
b_{\max}(\rho_{\mathrm{ini}} \to S_z) &= 1/2 \\
b_{\min}(\rho_{\mathrm{ini}} \to S_z) &= -1/2
\end{aligned} \tag{71}
$$

Hence, the achievable magnetization yield on the X-spins may in principle be doubled by breaking the spin system symmetry completely, as compared to the magnetically inequivalent AA′XX′ case.

This result may have relevance to SABRE technology [18, 19, 20, 21, 22]. Consider the high-field SABRE experiments described by Theis et al. [21]. Conversion of I-spin singlet order to S-spin magnetisation is achieved by implementing the following set of population transfers (in a reference frame rotated by $\pi/2$ so that the z-axis is parallel to the

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applied rf field, in the rotating frame):

$$
\begin{array}{rcll}
|S_0^{12}S_0^{23}> & \rightarrow & |T_0^{12}T_{+1}^{23}> & (g \rightarrow g) \\
|S_0^{12}T_{-1}^{23}> & \rightarrow & |T_0^{12}S_0^{23}> & (u \rightarrow u) \\
|S_0^{12}T_{+1}^{23}> & \rightarrow & |S_0^{12}T_{+1}^{23}> & (u \rightarrow u) \\
|S_0^{12}T_0^{23}> & \rightarrow & |S_0^{12}T_0^{23}> & (u \rightarrow u)
\end{array} \tag{72}
$$

The first two of the above population transfers are accomplished by allowing the spin dynamics to proceed in the presence of suitable resonance conditions. The last two transformations refer to level populations that are unchanged during the radiofrequency irradiation since no relevant resonance conditions are met. All of the above transformations occur within irreps of the magnetic inequivalence group $\mathcal{G}_{\text{MIE}}^{12,34}$, as indicated by the symmetry labels in equation 72.

A close examination of equation 72 shows that only the first transformation actually generates new S-spin magnetisation; the second transformation disables a term which would otherwise destructively interfere with the S-spin magnetisation already implicit in the third term, and the fourth transformation is neutral. Hence, this procedure does not fully make use of the parahydrogen spin order, and as discussed above, this defect is inevitable in a system of the form AA'XX'.

One possible set of population transformations which would double the resultant S-spin magnetisation in a SABRE experiment is as follows:

$$
\begin{array}{rcll}
|S_0^{12}S_0^{23}> & \rightarrow & |T_0^{12}T_{+1}^{23}> & (g \rightarrow g) \\
|S_0^{12}T_{-1}^{23}> & \rightarrow & |T_{-1}^{12}T_{+1}^{23}> & (u \rightarrow g) \\
|S_0^{12}T_{+1}^{23}> & \rightarrow & |S_0^{12}T_{+1}^{23}> & (u \rightarrow u) \\
|S_0^{12}T_0^{23}> & \rightarrow & |T_{+1}^{12}T_{+1}^{23}> & (u \rightarrow g)
\end{array} \tag{73}
$$

The first and third transformations are unchanged with respect to those in equation 72. The second and third transformations are new, and generate fresh S-spin magnetization (since they all involve populating the lower triplet state $|T_{+1}^{23}>$. However, these new transformations cross between the irreps of $\mathcal{G}_{\text{MIE}}^{12,34}$, and cannot be implemented without breaking chemical equivalence or the symmetry of the J-coupling network.

A practical implementation of equation 73, or other equivalent transformations in low-symmetry systems, has not yet been described.

[** To Here **]

6. Transformations of non-symmetric operators

The results given above apply to operators which commute with all members of the spin permutation group $\mathcal{G}$, and hence transform according to the fully symmetric irrep. What about other types of spin operators?

Just as sets of spin states may be constructed which span the irreps of the group $\mathcal{G}$, sets of spin operators which span the irreps may be constructed in similar fashion. Symmetrical operators which commute with all members of the permutation group belong to the fully symmetric irrep of the group.

As an example, consider a two spin-$\frac{1}{2}$ system. The operators for the sum and difference of the z-angular momenta are given by

$$
\begin{array}{rcl}
I_z & = & I_{1z} + I_{2z} \\
\Delta_z & = & I_{1z} - I_{2z}
\end{array} \tag{74}
$$

The operator I_z transforms according to the symmetric g representation of the permutation group $\mathcal{G}^{12}$. The difference operator Δ_z, on the other hand, transforms according to the antisymmetric u representation, as may be seen from the following transformation properties under the elements of $\mathcal{G}^{12}$:

$$
\begin{array}{rcl}
()\Delta_z()^{\dagger} & = & \Delta_z \\
(12)\Delta_z(12)^{\dagger} & = & -\Delta_z
\end{array} \tag{75}
$$

It is readily shown that operators which transform as different irreps of a group may not be interconverted by evolution under a symmetrical Hamiltonian. Hence, in the present case, the operators I_z and Δ_z are mutually isolated under an exchange-symmetric Hamiltonian – which is, in this case, intuitively obvious.

Operators which do transform according to the same irrep may in general be interconverted by a symmetrical Hamiltonian. If the interconverting operators both transform as the symmetrical irrep of the group, the results described above set the bounds on their mutual interconversion under unitary evolution. An open question concerns the bounds on the interconversion of two operators which both transform as the same irrep of the spin permutation group, but not the fully symmetric one. The bounds on such transformations are not known at the time of writing.

7. Conclusions

The bounds on unitary spin dynamics are defined by the eigenvalue spectra of the relevant operators, and the permutation symmetries of the spin Hamiltonians that drive the evolution. These general theoretical principles were developed many years ago [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12]. The current article has applied these principles to various situations in hyperpolarized NMR and some cases involving chemical and magnetic equivalence. In some cases non-obvious results are obtained, such as the impossibility of converting A-spin magnetization completely into X-spin magnetization in magnetically equivalent systems of the form A_2X_2. In addition it is found that the use of chemically equivalent four-spin systems of the type $AA'XX'$ may lead to non-optimal efficiency in implementations of the SABRE hyperpolarization method. Our group is now applying these results to an analysis of the conditions under which long-lived states may be generated and are accessible to observation, in a variety of spin systems with different symmetries.

Acknowledgments

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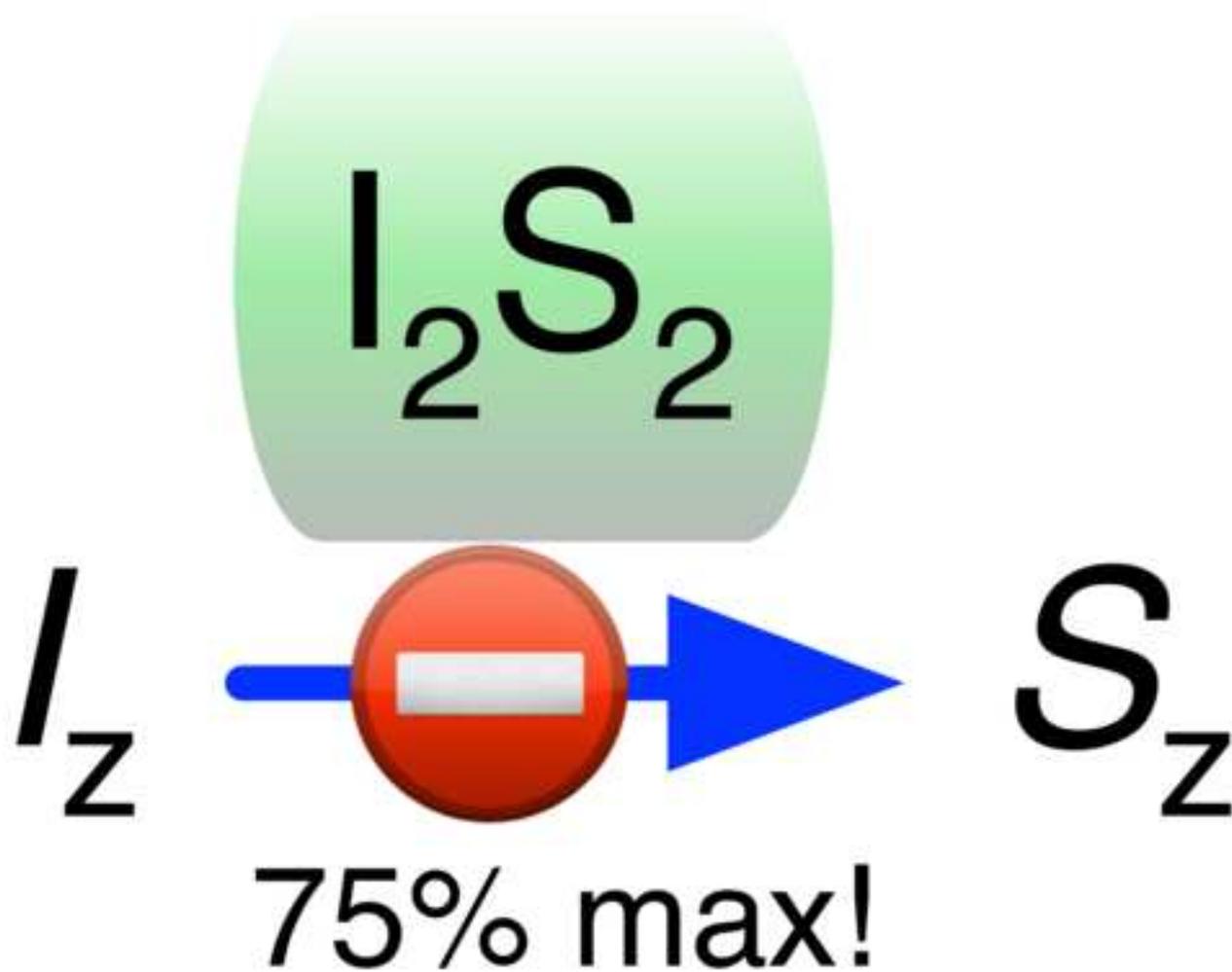
- Spin dynamics is constrained by permutation symmetry.
- The bounds may be derived using irreducible representations of the permutation group.
- Magnetic equivalence can make some transformations impossible to achieve.
- Symmetry-breaking may be needed for maximum efficiency.