Rotational-permutational dual-pairing and long-lived spin order

Christian Bengs[1, a)]

School of Chemistry, Southampton

Quantum systems in contact with a thermal environment experience coherent and incoherent dynamics. These drive the system back towards thermal equilibrium after an initial perturbation. The relaxation process involves the reorganisation of spin state populations and the decay of spin state coherences. In general individual populations and coherences may exhibit different relaxation time constants. Particular spin configurations may exhibit exceptionally long relaxation time constants. Such spin configurations are known as long-lived spin order. The existence of long-lived spin order is a direct consequence of the symmetries of the system. For nuclear spin systems rotational and permutational symmetries are of fundamental importance. Based on the Schur-Weyl duality theorem we describe a theoretical framework for the study of rotational and permutational dual-symmetries in the context of long-lived spin order. Making use of the proposed formalism we derive exact bounds on the number on long-lived spin populations and coherences for systems exhibiting rotational-permutational dual-symmetries.

[a)]cb2r15@soton.ac.uk

I. INTRODUCTION

The term long-lived nuclear spin order refers to particular configurations of the spin ensemble that exhibit exceptionally long relaxation times[1,2]. These may either be formed by spin populations or spin coherences[1–20]. In both instances the relaxation time of these configurations may greatly exceed the conventional relaxation time constant T_1. For this reason long-lived nuclear spin order has been found useful for a variety of practical applications including diffusion processes, bio-molecular ligand-binding, para-hydrogen induced hyperpolarisation and quantum computing[21–31].

Spin configurations with exceptional lifetimes arise if the system exhibits a certain degree of symmetry. The application of symmetry arguments for the description of NMR experiments has a longstanding history[19,32–43]. It is therefore not too surprising that the theory of long-lived nuclear spin order is most naturally formulated within a group theoretical framework. Here the collection of symmetry operations that leave the system invariant form a mathematical group G[44–47]. The symmetries of the system may then be studied by making use of fundamental results from group theory[4–6,14–19,48]. Most importantly the presence of symmetries implies the existence of selection rules which may be determined by the generalised Wigner-Eckart-Theorem[46,47]. The underlying Hilbert space $\mathbb{H}$ then decomposes into a direct sum of irreducible representation Γ_j of the group G. Groups of special interest for NMR applications are the three-dimensional rotation group SO(3) and the symmetric group S_n[3–5,14–19,36,38,39].

Exceptional relaxation time constants follow from symmetry induced selection rules that either forbid or greatly suppress transitions between different symmetry manifolds by coherent and incoherent mechanisms[3–8,14–18]. As a consequence information across different symmetry manifolds may be stored for an extended period of time. Meaningful long-lived spin order may then be defined as the population difference across distinct symmetry manifolds[3,14–18,48]. In the case of two coupled spin-1/2 particles for example a long-lived state may be defined as the population imbalance between the anti-symmetric singlet and symmetric triplet manifold[12].

In more complicated spin systems an intuitive argument to determine the number of long-lived spin order becomes increasingly difficult. Some long-lived spin operators for particular spin systems have been reported previously[4,5,14–18,49–55]. Recently references 16 and 56 have

given a lower bound on the number of long-lived spin populations based on group theoretical arguments. Long-lived spin populations may be constructed from a set of projection operators P^{Γ_j} that project onto the different symmetry manifolds Γ_j of a group G. The number of non-trivial long-lived spin operators is bounded by the relation[16]

$$N_{\mathrm{LLS}} \geq N_\Gamma - 1, \tag{1}$$

where N_Γ represents the number of irreducible representations of G.

This bound however displays some issues. Consider the following (apparent) paradox: The three protons of a methyl rotor constitute a system of three identical spin-1/2 particles. In a typical solution state NMR experiment the symmetry of the methyl group is commonly described by the alternating group of order three A_3[14–17,37]. The group A_3 may be characterised by three irreducible representations: $\{A, E_a, E_b\}$ leading to $N_\Gamma = 3$. It is however straightforward to show that the symmetry of the spin Hamiltonian for the methyl protons is equally well described by the symmetric group of order three S_3. The group S_3 is similarly characterised by three irreducible representations: $\{A_1, A_2, E\}$. Spin functions for three identical spin-1/2 particles however are not capable of supporting the A_2 irreducible representation[44–47]. This reduces the number of available irreducible representations by one, so that $N_\Gamma = 2$. As a consequence the number of long-lived spin operators predicted by characterisation according to A_3 or S_3 symmetry are not the same. This has lead to some confusion regarding which symmetry group of the Hamiltonian should be used to describe the system.

In this paper we address and resolve this issue by treating rotational and permutational symmetries on equal footing. This is done by exploiting the dual-pairing for the irreducible representations of the unitary group $U(n)$ and the symmetric group S_n. The intimate relationship between these two groups is described by the Schur-Weyl duality theorem[57,58]. The Schur-Weyl duality theorem gives a concrete relation between the irreducible representations of S_n and $U(n)$. Since the three-dimensional rotation group is a subgroup of the unitary group $U(n)$ the duality principle provides a connection between the irreducible representations of S_n and $SO(3)$. This may be done by utilising branching rules for irreducible representations for the subgroup chain $SO(3) \subset U(n)$. This way we will be able to state a new lower bound on the number of long-lived spin operators including spin populations and coherences.

For practical applications a simple approach is outlined to construct basis sets that possess dual-symmetry for any two commuting groups G_a and G_b and in particular the case $G_a = \mathrm{S}_n$ and $G_b = \mathrm{SO}(3)$ is treated. Such basis sets may be used to verify the presented results and simplify explicit calculations of relaxation dynamics. We illustrate this by reexamining the long-lived states of a methyl rotor under dual-selection rules. A detailed application to practical NMR examples however is beyond the scope of this paper and deferred to a future publication currently under preparation.

II. BACKGROUND

A short overview of key concepts and necessary terminology is given in order to facilitate the following discussion. The required group theoretical concepts are presented in full detail in references 44, 46 and 47.

A. Groups and Subgroups

Consider a set of elements G equipped with a composition law $(*)$ for any two elements $g_i, g_j \in G$. The composition law is often abbreviated by *group product* or simply *product*. If $(G, *)$ satisfies the axioms:

- The product $g_i * g_j$ is an element of G for all elements $g_i, g_j \in G$.

- The product of the group elements $g_i * g_j * g_k$ is associative.

- The identity element denoted by e is an element of the group G.

- For every element g_i there exists the corresponding inverse element $g_i^{-1} \in G$ so that $g_i * g_i^{-1}$ equals the identity element e in G.

the set G together with $(*)$ forms a *group*[44–47].

If the group G contains a subset A so that A fulfills the group axioms, the subset A is called a *subgroup* of G. Subgroups are commonly denoted by $A \subset G$. In general A may contain additional subgroups leading to a so-called *subgroup chain*, $A_N \subset \cdots \subset A_2 \subset A_1 \subset G$, where N is the length of the subgroup chain[47].

B. Symmetric group

The *symmetric group* naturally arises in physical systems consisting of a set of identical particles. Consider a set of N elements $\Omega_N = \{1, 2, \ldots, N\}$. A *permutation* is as a *re-arrangement* of elements in Ω_N in a one-to-one manner[44]. For example if Ω_N is given by $\{1, 2, 3\}$ a permutation may be defined as follows:

$$\sigma : 1 \mapsto 2, 2 \mapsto 3, 3 \mapsto 1. \tag{2}$$

This sequence of operations is often abbreviated by the so-called *cycle notation*

$$\sigma = (123). \tag{3}$$

The collection of all such permutations on the set Ω_N satisfies the group axioms and forms a group G of order $N!$. The resulting group is called the symmetric group of order $N!$ and denoted by S_n.

A simple example is the symmetric group on a set of two objects denoted by S_2. The $2! = 2$ elements of S_2 are given by

$$S_2 = \{(1)(2), (12)\} = \{e, (12)\}, \tag{4}$$

where the permutation $(1)(2)$ is the identity element in S_2 and in general $(1)(2)\ldots(n) = e$ in S_n. The symmetric group on a set of three objects is denoted by S_3 and has $3! = 6$ elements

$$S_3 = \{e, (12), (23), (13), (123), (132)\}. \tag{5}$$

The symmetric group S_3 is the first symmetric group that contains a non-trivial subgroup. This subgroup is the set of all even permutations

$$A_3 = \{e, (123), (132)\}. \tag{6}$$

In general the set of all even permutations on a set of order N is called the *alternating group* $A_n \subset S_n$. The alternating group A_3 is commonly used to analyse the dynamics and describe symmetries of methyl group rotors[14–16,18,37,59]. In the NMR literature however it is common practice to refer to the groups S_3 and A_3 by the crystallographic point groups C_{3v} and C_3. This is possible since the groups $S_3 \cong C_{3v}$ and $A_3 \cong C_3$ are isomorphic to each other.

C.   Dynamic groups

The *unitary group* $U(n)$ consists of all $n \times n$ matrices that satisfy the condition

$$U^\dagger U = \mathbb{1}, \tag{7}$$

so that U^{-1} equals its conjugate transpose or adjoint denoted by $U^\dagger$. The unitary group $U(n)$ forms a connected continuous group of n^2 parameters[44,46]. Group elements of $U(n)$ may be generated as follows

$$u = \exp\left\{ -i \sum_{j=1}^{n^2} \alpha_j E_j \right\}, \tag{8}$$

with α_j being a real number and E_j a $n \times n$ hermitian matrix that belongs to corresponding Lie algebra $\mathfrak{u}(n)$.

An important subgroup of the unitary group is the *special unitary* group $SU(n) \subset U(n)$. Elements of $SU(n)$ fulfill the additional constraint $\det(U) = 1$. The group elements of $SU(n)$ are generated by $n^2 - 1$ traceless hermitian matrices[44,46]

$$su = \exp\left\{ -i \sum_{j=1}^{n^2-1} \alpha_j T_j \right\} \quad \text{with} \quad \mathrm{Tr}(T_j) = 0. \tag{9}$$

The generators of the Lie algebra $\mathfrak{su}(n)$ may be chosen to be polynomials in the Cartesian angular momentum operators $\{I_x, I_y, I_z\}$, which naturally arise in the definition of a spin Hamiltonian[60–63].

The three-dimensional *rotation group* $SO(3) \subset SU(n) \subset U(n)$ plays a central role in NMR theory[40,49,50,64–71]. From an experimental point of view $SO(3)$ group elements may be generated either by physical rotations of the sample or application of suitable radio-frequency pulses[60,63]. The elements of $SO(3)$ may be specified by a rotation axis $\mathbf{n}$ and a rotation angle θ:

$$R(\mathbf{n}, \theta) = \exp\left\{ -i\theta \mathbf{n} \cdot \mathbf{I} \right\}, \quad \mathbf{I} = \begin{bmatrix} I_x & I_y & I_z \end{bmatrix}, \quad \mathbf{n} = \begin{bmatrix} n_x & n_y & n_z \end{bmatrix}, \quad \mathbf{n} \cdot \mathbf{n} = 1. \tag{10}$$

An alternative parametrisation frequently found in the NMR literature is the *Euler angle* convention. Here group elements of $SO(3)$ are specified by a set of three rotation angles $\{\alpha, \beta, \gamma\}$[60–63]. A generic group element may then be expressed as follows

$$R(\alpha, \beta, \gamma) = R_z(\alpha) R_y(\beta) R_z(\gamma) = \exp\left\{ -i\alpha I_z \right\} \exp\left\{ -i\beta I_y \right\} \exp\left\{ -i\gamma I_z \right\}. \tag{11}$$

The Euler angle parametrisation has been used extensively for the description of rotating solids, the design of composite pulses, decoupling schemes and phase cycles[40,49–55,66,67].

D. Conjugacy classes

The elements of a group G may be partitioned into *conjugacy classes*. Two elements g_i and g_j of G are conjugate to each other if the following relation holds

$$g_i = g_k g_j g_k^{-1} \quad \text{for some} \quad g_k \in G. \tag{12}$$

The set of all elements conjugate to each other is called a *conjugacy class*

$$\text{Cl}(g_i) = \{g_j \mid g_i = g_k g_j g_k^{-1} \text{ for some } g_k \in G\} \tag{13}$$

and g_i is called the *representative* of the class.

For the symmetric group elements with the same cycle structure form a conjugacy class[44]. For example the elements (123) and (132) and the elements $(12)(34)$ and $(13)(24)$ are conjugate to each other. More generally the conjugacy classes of S_n may be specified by a string of cycle lengths. For the group S_3 this means

$$
\begin{aligned}
\text{Cl}(e = (1)(2)(3)) &= [111], \\
\text{Cl}((12)(3)) &= [21], \quad \text{Cl}((123)) = [3].
\end{aligned}
\tag{14}
$$

The possible cycle structures for S_n may be determined by considering all *integer partitions* λ of n[72]. The symbol $\lambda \vdash n$ will be reserved to indicate that λ partitions n. An integer partition of n represents n as a sum of one or more positive integers. The integer partitions of 5 for example are given by

$$
\begin{aligned}
5 &\mapsto [5], \quad 4+1 \mapsto [41], \quad 3+1+1 \mapsto [311], \\
2+1+1+1 &\mapsto [2111], \quad 1+1+1+1+1 \mapsto [11111], \\
3+2 &\mapsto [32], \quad\quad\quad\quad 2+2+1 \mapsto [221].
\end{aligned}
\tag{15}
$$

Thus there is a natural identification between conjugacy classes of S_n and the integer partitions of n.

The conjugacy classes for matrix groups such as $\text{U}(n)$, $\text{SU}(n)$ and $\text{SO}(3)$ are formed by all matrices that are related to each other by a *similarity transformation*

$$\text{Cl}(A) = \{B \mid A = V B V^\dagger \text{ for some } V \in \text{U}(n), \text{SU}(n), \text{SO}(3)\}. \tag{16}$$

Since the trace of a matrix is preserved under a similarity transformation the conjugacy classes are given by all matrices with the same trace. For the rotation group the conjugacy

classes are formed by all rotations with the same effective rotation angle θ. Conjugate rotations then simply correspond to the same rotation as viewed from different reference frames.

E. Irreducible representations

For certain applications it is convenient to generate a representation $D(g)$ for the group elements $g \in G$. This is done by mapping the group elements onto $(d \times d)$ dimensional matrices. The group composition law then translates into matrix multiplication. If the mapping is additionally one-to-one the representation is said to be *faithful*.

For groups considered here there always exists a similarity transformation V that block-diagonalises the representations $D(g)$ simultaneously so that all $D(g) \; \forall g \in G$ admit a direct sum decomposition in $\mathbb{H}$

$$V D(g) V^{\dagger} = \bigoplus_{j=1}^{N_{\Gamma}} m_{\Gamma_j} D^{\Gamma_j}(g) \quad \forall g \in G. \tag{17}$$

The resulting $(d_{\Gamma_j} \times d_{\Gamma_j})$ dimensional representations $D^{\Gamma_j}(g)$ are called *irreducible representations* of G and are labelled by Γ_j. The total number of irreducible representations for a given group G is denoted by N_{Γ}. An important theorem of representation theory states that the number of irreducible representations N_{Γ} of a group G is equal to the number of conjugacy classes of G[44–47].

Depending on the underlying Hilbert space $\mathbb{H}$ some irreducible representation may appear multiple times and some may not appear at all. The *multiplicity* of a given irreducible representation is denoted by m_{Γ_j}. The dimension of the Hilbert space $\mathbb{H}$ may then be expressed as follows

$$d_{\mathbb{H}} = \sum_{j=1}^{N_{\Gamma}} m_{\Gamma_j} d_{\Gamma_j}. \tag{18}$$

The basis set that spans the irreducible representations of a given group G is called a *symmetry adapted basis* $\mathcal{B}_G$. The members of $\mathcal{B}_G$ may be specified by a set of *group labels*[46,47]

$$\mathcal{B}_G = \{|\Gamma_j, \gamma, \mu\rangle\}. \tag{19}$$

The first label Γ_j specifies the irreducible representation the state belongs to. The second label γ distinguishes between basis elements belonging to the same irreducible representation

with $d_{\Gamma_j} > 1$. In this work we will refer to this label as the *group projection number*. The label μ is necessary for $m_{\Gamma_j} > 1$ to uniquely address each basis element.

This notation is chosen to resemble the labelling of angular momentum states $|I, m\rangle$ with the addition of a multiplicity label.

F. Characters

The irreducible representations of a group may be classified according to their *characters*. The character χ of a representation is given by the trace of the corresponding matrix

$$\chi(g) = \text{Tr}(D(g)). \tag{20}$$

From equation 17 it follows that the character $\chi(g)$ may be expressed as follows

$$\chi(g) = \sum_{j=1}^{N_\Gamma} m_{\Gamma_j} \text{Tr}(D^{\Gamma_j}(g)) = \sum_{j=1}^{N_\Gamma} m_{\Gamma_j} \chi^{\Gamma_j}(g). \tag{21}$$

The characters $\chi^{\Gamma_j}(g)$ are called *irreducible characters* of $g \in G$. The irreducible characters are orthogonal to each other with respect to the following complex inner product

$$\frac{1}{|G|} \sum_{g \in G} (\chi^{\Gamma_j}(g))^* \chi^{\Gamma_k}(g) = \delta_{jk}. \tag{22}$$

This is a consequence of the Schur orthogonality relations[44–47]

$$\sum_{g \in G} [D^{\Gamma_j}(g)]^*_{mn} [D^{\Gamma_k}(g)]_{m'n'} = \delta_{jk} \delta_{mm'} \delta_{nn'} \frac{|G|}{d_{\Gamma_i}} \tag{23}$$

for the matrix elements $[D^{\Gamma_j}(g)]_{mn}$ of the irreducible representation Γ_j. An irreducible representation Γ_j is therefore uniquely specified by its set of characters.

The characters are conveniently collected into a *character table*. An example of a typical character table is given in table I.

The first column runs through all irreducible representations of the group. The following columns are labelled by the group elements of G.

1. Symmetric group

According to section II E the number of irreducible representations equals the number of conjugacy classes. For S_n the conjugacy classes are in a one-to-one correspondence with

Γ_j	e	g_1	$\cdots$	$g_{|G|}$
Γ_1	$\chi^{\Gamma_1}(e)$	$\chi^{\Gamma_1}(g_2)$	$\cdots$	$\chi^{\Gamma_1}(g_{|G|})$
Γ_2	$\chi^{\Gamma_2}(e)$	$\chi^{\Gamma_2}(g_2)$	$\cdots$	$\chi^{\Gamma_2}(g_{|G|})$
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
Γ_{N_Γ}	$\chi^{\Gamma_{N_\Gamma}}(e)$	$\chi^{N_\Gamma}(g_2)$	$\cdots$	$\chi^{N_\Gamma}(g_{|G|})$

Table I. Character table of a generic group G.

the integer partition of n (see section II D). As a result the irreducible representations of S_n may also be labelled by integer partitions.

It is common to represent the irreducible representation of S_n by the integer partitions and the classes by a cycle representative. In the case of S_3 this results in a character table as indicated in table II.

Γ_j	e	$(12)(3)$	$(13)(2)$	$(23)(1)$	(123)	(132)
Γ_1=[3]	1	1	1	1	1	1
Γ_2=[111]	1	-1	-1	-1	1	1
Γ_3=[21]	2	-1	-1	-1	0	0

Table II. Character table for the group S_3.

The assignment of a given integer partition to an irreducible representations follows particular symmetry arguments that may be found in reference 44.

2. Three-dimensional rotation group

The character table for SO(3) may be determined by considering solutions of the three-dimensional Laplace equation

$$\frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} = 0. \tag{24}$$

The solutions to this equation are spherical harmonics $Y_{lm}(\theta, \phi)$[46,47]. These span a $(2l+1)$ dimensional representation of SO(3). By the similarity argument of section II D it is sufficient to consider rotations around the z-axis to determine the characters. The resulting

character table for the group SO(3) is given by table III.

Γ_j	e	$R(\mathbf{n}, \theta)$
l	1	$\sin((l + \frac{1}{2})\theta)/\sin(\frac{1}{2}\theta)$

Table III. Character table for the group SO(3).

The irreducible representations of SO(3) are thus distinguished by the quantum number l. The spherical harmonics $Y_{lm}(\theta, \phi)$ are additionally labelled by a quantum number m to distinguish elements with the same quantum number l but different transformation properties under the two-dimensional rotation group SO(2).

G.   Direct product groups

Given two groups G_a and G_b one may define the *direct product* group $G_a \otimes G_b$ by introducing the following element-wise operation[44–47]

$$(g_i^a, g_j^b) * (g_k^a, g_l^b) = (g_i^a *_a g_k^a, g_j^b *_b g_l^b), \quad \forall g_i^a, g_k^a \in G_a \quad \text{and} \quad \forall g_j^b, g_l^b \in G_b, \tag{25}$$

where $(*_a)$ and $(*_b)$ are the group products for G_a and G_b, respectively. The direct product group $G_a \otimes G_b$ contains subgroups G_a' and G_b' which are isomorphic to $G_a \cong G_a'$ and $G_b \cong G_b'$. The isomorphism may be constructed as follows

$$G_a \cong G_a' = \{(g^a, e^b)\}, \quad G_b \cong G_b' = \{(e^a, g^b)\}, \tag{26}$$

so that the two groups G_a' and G_b' commute

$$[G_a', G_b'] = 0 \tag{27}$$

and every element of $G_a \otimes G_b$ may be represented as a product of an element from G_a' and G_b'.

If both groups G_a and G_b are realised in terms of representations $D(g^a)$ and $D(g^b)$ the direct product group may be constructed by forming the *Kronecker product* of the matrices $D(g^a)$ and $D(g^b)$

$$D(g^a, g^b) = D(g^a) \otimes D(g^b). \tag{28}$$

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III. LONG-LIVED SPIN ORDER

A. General framework

We consider a system of N identical spins with quantum number I. A single particle state occupies a Hilbert space $\mathbb{H}_{2I+1}$ with dimension $d_I = 2I+1$. The state of the composite system $|\psi\rangle$ is an element of the composite Hilbert space $\mathbb{H}$ given by the N-fold tensor product of the Hilbert space $\mathbb{H}_{2I+1}$ with dimension $d_{\mathbb{H}} = (2I+1)^N$

$$\mathbb{H} = \underbrace{\mathbb{H}_{2I+1} \otimes \cdots \otimes \mathbb{H}_{2I+1}}_{N-\text{times}}. \tag{29}$$

We further assume that we are dealing with an ensemble of such systems dissolved in a liquid. The state may then be described by a density operator ρ

$$\rho = \overline{|\psi\rangle\langle\psi|}, \tag{30}$$

where the overbar indicates an average across the spin-ensemble. The density operator ρ is an element of the space of linear operators on $\mathbb{H}$ denoted by $\mathbb{L}(\mathbb{H})$

$$\mathbb{L}(\mathbb{H}) = \mathbb{H} \otimes \mathbb{H}^* = \underbrace{\mathbb{H}_{2I+1} \otimes \cdots \otimes \mathbb{H}_{2I+1}}_{N-\text{times}} \otimes \underbrace{\mathbb{H}_{2I+1}^* \otimes \cdots \otimes \mathbb{H}_{2I+1}^*}_{N-\text{times}}. \tag{31}$$

In the NMR jargon $\mathbb{L}(\mathbb{H})$ is known as *Liouville space*[61]. Making use of superoperator notation the Liouville-von-Neuman equation governing the dynamics of the ensemble may be expressed as follows[73]

$$\frac{d}{dt}|\rho(t)) = (\hat{\mathcal{L}}_{\text{coh}} + \hat{\mathcal{R}}^{\text{lab}})|\rho(t)), \tag{32}$$

with $\hat{\mathcal{L}}_{\text{coh}}$ being the coherent Liouvillian of the system, $\hat{\mathcal{R}}^{\text{lab}}$ the generator of relaxation expressed in the laboratory frame and $|Q)$ denotes a state in $\mathbb{L}(\mathbb{H})$. The coherent Liouvillian is assumed to be the same for each member of the ensemble and is given by the commutation superoperator of $\mathcal{H}_{\text{coh}}$

$$\hat{\mathcal{L}}_{\text{coh}} = -i(\mathcal{H}_{\text{coh}} \otimes \mathbb{1} - \mathbb{1} \otimes \mathcal{H}_{\text{coh}}^{\dagger}). \tag{33}$$

The assumption of an ensemble of N identical spins dissolved in an isotropic liquid allows us to express the coherent Hamiltonian as follows[61–63]

$$\mathcal{H}_{\text{coh}} = \omega_0 I_z + 2\pi J \sum_{i<j}^{N} \mathbf{I}_i \cdot \mathbf{I}_j \quad \text{with} \quad \mathbf{I}_i = \begin{bmatrix} I_{ix} & I_{iy} & I_{iz} \end{bmatrix}, \tag{34}$$

with I_z being the total z-angular momentum operator. The interaction between the spins and the magnetic field is characterised by a single Larmor frequency ω_0. The second term describes the mutual scalar coupling between pairs of spins with the same coupling strength J.

The relaxation superoperator $\hat{\mathcal{R}}^{\text{lab}}$ may be constructed from the fluctuating part of the spin Liouvillian $\hat{\mathcal{L}}_{\text{fluc}}(t)$

$$\hat{\mathcal{L}}_{\text{fluc}}(t) = -i\hat{\mathcal{H}}_{\text{fluc}}(t). \tag{35}$$

The fluctuating part is in general different for each member of the ensemble at given point it time. For conventional spin systems the relaxation superoperator $\hat{\mathcal{R}}^{\text{lab}}$ takes the form of a double commutation superoperator[61,62]

$$\hat{\mathcal{R}}^{\text{lab}} = \int_{-\infty}^{0} \overline{\hat{\tilde{\mathcal{L}}}_{\text{fluc}}(0)\hat{\tilde{\mathcal{L}}}_{\text{fluc}}(\tau)}d\tau, \tag{36}$$

where $\hat{\tilde{\mathcal{L}}}_{\text{fluc}}(t)$ represents the fluctuating part expressed in the interaction frame of the coherent Liouvillian

$$\hat{\tilde{\mathcal{L}}}_{\text{fluc}}(t) = \exp\left\{-\hat{\mathcal{L}}_{\text{coh}}t\right\}\hat{\mathcal{L}}_{\text{fluc}}(t)\exp\left\{+\hat{\mathcal{L}}_{\text{coh}}t\right\}. \tag{37}$$

The relaxation superoperator for spin systems deviating strongly from thermal equilibrium should be formulated within the Lindblad formalism[74,75]. The symmetry properties of the relaxation superoperator do not depend upon this choice and we will avoid this complication here.

B.   Rotational symmetries

An operator Q possesses rotational symmetry if it is invariant under conjugation by elements of SO(3)

$$R^{\dagger}(\mathbf{n}, \theta)QR(\mathbf{n}, \theta) = Q. \tag{38}$$

Being invariant under rotations implies that Q preserves the total angular momentum I and z-angular momentum m of a state in $\mathbb{H}$.

The coherent Hamiltonian $\mathcal{H}_{\text{coh}}$ is in general not invariant under SO(3) but commutes with the total angular momentum operator I^2 and the total z-angular momentum operator I_z

$$[I^2 + I_z, \mathcal{H}_{\text{coh}}] = 0, \tag{39}$$

where I^2 and I_z are defined as follows:

$$I_z = \sum_i^N I_{iz}, \quad I^2 = \sum_{i,j}^N \mathbf{I}_i \cdot \mathbf{I}_j \quad \text{with} \quad \mathbf{I}_i = \begin{bmatrix} I_{ix} & I_{iy} & I_{iz} \end{bmatrix}. \tag{40}$$

As a consequence the coherent Hamiltonian also preserves total angular momentum I and z-angular momentum m, and eigenstates of $\mathcal{H}_{\text{coh}}$ may be chosen to be total angular momentum states $|I, m\rangle$

$$(I^2 + I_z)|I, m\rangle = (I(I+1) + m)|I, m\rangle. \tag{41}$$

The set of all angular momentum states $|I, m\rangle$ forms a symmetry adapted basis $\mathcal{B}_{\text{SO(3)}}$ for rotations in $\mathbb{H}$

$$\mathcal{B}_{\text{SO(3)}} = \{|I, m\rangle\}. \tag{42}$$

Similarly, the total angular momentum superoperator $\hat{I}^2$ and total z-angular momentum superoperator $\hat{I}_z$ in $\mathbb{L}(\mathbb{H})$ are given by the expressions below

$$\hat{I}_z = \sum_i^N \hat{I}_{iz}, \quad \hat{I}^2 = \sum_{i,j}^N \hat{\mathbf{I}}_i \cdot \hat{\mathbf{I}}_j \quad \text{with} \quad \hat{\mathbf{I}}_i = \begin{bmatrix} \hat{I}_{ix} & \hat{I}_{iy} & \hat{I}_{iz} \end{bmatrix}. \tag{43}$$

The eigenoperators of $(\hat{I}^2, \hat{I}_z)$ are given by *irreducible spherical tensor operators* (ISTO)[60]. Each ISTO may be labelled by two quantum numbers (k, m) which reflect their symmetry under SO(3) and SO(2) operations

$$(\hat{I}^2 + \hat{I}_z)|T_{km}) = (k(k+1) + m)|T_{km}). \tag{44}$$

The set of all spherical tensor $|T_{km})$ forms a symmetry adapted basis $\hat{\mathcal{B}}_{\text{SO(3)}}$ for rotations in $\mathbb{L}(\mathbb{H})$

$$\hat{\mathcal{B}}_{\text{SO(3)}} = \{|T_{km})\}. \tag{45}$$

Consider the coherent Liouvillian resulting from the Hamiltonian in equation 34. It is straightforward to show that $\hat{\mathcal{L}}_{\text{coh}}$ commutes with $\hat{I}^2$ and $\hat{I}_z$

$$[\hat{I}^2 + \hat{I}_z, \hat{\mathcal{L}}_{\text{coh}}] = 0. \tag{46}$$

The coherent Liouvillian $\hat{\mathcal{L}}_{\text{coh}}$ thus preserves the two quantum numbers (k, m) and its representations may be decomposed according to the irreducible representations of the rotation group SO(3).

The relaxation superoperator $\hat{\mathcal{R}}^{\text{lab}}$ on the other hand possesses no symmetry in general. But the combination of dominant Zeeman interactions and weak relaxation processes driven by rotational Brownian motion imposes symmetry onto the relaxation superoperator[64,65]. Typically $\hat{\mathcal{R}}^{\text{lab}}$ is well approximated by a secularised relaxation superoperator $\hat{\mathcal{R}}$ which possesses at least SO(2) symmetry

$$[\hat{I}_z, \hat{\mathcal{R}}] = 0, \tag{47}$$

so that $\hat{\mathcal{R}}$ preserves the z-angular momentum of any ISTO. Without any further approximations or assumptions $\hat{\mathcal{R}}$ may not be decomposed into a sum of irreducible representations of the rotation group SO(3).

C.   Permutational symmetries

A system of N identical spins possesses *spin permutation* symmetry. The action of a spin permutation P_σ onto a direct product state $|\psi_1\psi_2\ldots\psi_N\rangle$ may be expressed as shown below

$$P_\sigma|\psi_1\psi_2\ldots\psi_N\rangle = |\psi_{\sigma(1)}\psi_{\sigma(2)}\ldots.\psi_{\sigma(N)}\rangle. \tag{48}$$

For instance, the permutation P_{12} acting on the state $|\psi_1\psi_2\psi_3\rangle$ leads to the following

$$P_{12}|\psi_1\psi_2\psi_3\rangle = |\psi_2\psi_1\psi_3\rangle. \tag{49}$$

The action of a spin permutation P_σ onto an operator Q is given by conjugation of Q by P_σ

$$P_\sigma : Q \mapsto P_\sigma Q P_\sigma^\dagger. \tag{50}$$

When an operator is expressed in terms of Cartesian angular momentum operators for example, a spin permutation amounts to a permutation of the indices

$$P_{12}I_{1x}I_{2y}P_{12}^\dagger = I_{2x}I_{1y}. \tag{51}$$

Consider the coherent Hamiltonian of equation 34. Since the nuclear Larmor frequency ω_0 and the mutual scalar coupling constant J is the same for all members of the system, the coherent Hamiltonian is invariant under the symmetric group S_n

$$P_\sigma \mathcal{H}_{\text{coh}} P_\sigma^\dagger = \mathcal{H}_{\text{coh}} \quad \forall \sigma \in S_n. \tag{52}$$

Similarly, the coherent Liouvillian $\hat{\mathcal{L}}_{\text{coh}}$ is invariant under the set of spin permutation super-operators

$$\hat{P}_\sigma = P_\sigma \otimes P_\sigma^*, \tag{53}$$

that generate a representation of the group S_n on $\mathbb{L}(\mathbb{H})$

$$\hat{P}_\sigma \hat{\mathcal{L}}_{\text{coh}} \hat{P}_\sigma^\dagger = \hat{\mathcal{L}}_{\text{coh}} \quad \forall \sigma \in S_n. \tag{54}$$

As a consequence the representations of $\mathcal{H}_{\text{coh}}$ and $\hat{\mathcal{L}}_{\text{coh}}$ may be decomposed according to irreducible representations of S_n. And again without further approximations $\hat{\mathcal{R}}$ does not possess any spin permutation symmetry.

D. Schur-Weyl duality

Sections III B and III C showed that the coherent Liouvillian and Hamiltonian given by equations 33 and 34 are invariant under group elements S_n and preserve total and z- angular momentum. This gives rise to the concept of a *dual-symmetry*[57,58]. Consider a Hamiltonian $\mathcal{H}$ or Liouvillian $\hat{\mathcal{L}}$ that commutes with two groups G_a and G_b

$$\begin{aligned}
[\mathcal{H}, G_a] &= 0, & [\mathcal{H}, G_b] &= 0, \\
[\hat{\mathcal{L}}, G_a] &= 0, & [\hat{\mathcal{L}}, G_b] &= 0,
\end{aligned} \tag{55}$$

with the additional assumption that G_a and G_b commute

$$[G_a, G_b] = 0. \tag{56}$$

It is easy to check that that this condition is fulfilled for spin rotations and permutations. In this case one speaks of a dual-symmetry and there exists a set of basis states and basis operators that transforms irreducibly under G_a and G_b simultaneously. Similar to equation 19 the basis elements may then be specified by a set of two group labels[47]

$$\begin{aligned}
\mathcal{B}_{G_b}^{G_a} &= \{|\Gamma_j^a, \gamma_a, \mu_a, \Gamma_k^b, \gamma_b, \mu_b\rangle\}, \\
\hat{\mathcal{B}}_{G_b}^{G_a} &= \{|\Gamma_j^a, \gamma_a, \mu_a, \Gamma_k^b, \gamma_b, \mu_b\rangle\}.
\end{aligned} \tag{57}$$

In general there is no special relationship between the irreducible representations of G_a and G_b. An exception exists for the case that $G_a = U(n)$ and $G_b = S_n$. The connection between irreducible representations of $U(n)$ and S_n is described by the Schur-Weyl duality

theorem[57,58]. Following reference 58, a simplified version of this theorem states that the direct product representation of $U(n)$ and S_n may be used to decompose $\mathbb{H}$ according to the irreducible representations $\{\lambda\}$ of $U(n)$ and $[\lambda]$ of S_n as follows

$$\mathbb{H} = \bigoplus_{\lambda \vdash N}^{l(\lambda) \leq n} D^{\{\lambda\}} \circ D^{[\lambda]}, \tag{58}$$

where $l(\lambda)$ indicates the length of a partition and we denote the dual pairing by $(\circ)$. There is thus a unique pairing between irreducible representations of $U(n)$ and S_n identified by a common partition λ.

The Schur-Weyl duality further ensures (not captured by equation 58) that the multiplicity $m_{\{\lambda\}}$ of an irreducible representation of $U(n)$ is the same as the dimensionality $d_{[\lambda]}$ of the corresponding irreducible representation of S_n and vice versa.

Since the rotation group $SO(3)$ is a subgroup of $U(n)$ the Schur-Weyl duality theorem provides a way to identify irreducible representations of $SO(3)$ with those of S_n. Strictly speaking this only holds in $\mathbb{H}$ and we briefly outline how to extend the duality principle to $\mathbb{L}(\mathbb{H})$ in appendix A 3.

To illustrate implications of the Schur-Weyl duality we first consider Hilbert spaces of spin-1/2 systems. The irreducible representations of $U(2)$ remain irreducible upon restriction to $SO(3)$. In this case the branching rules simplify significantly[44,45].

The coupled angular momentum basis for a system of two spin-1/2 particles consists of three triplet states $|T_{1m}\rangle$ with $I = 1$ and a singlet state $|S_{00}\rangle$ with $I = 0$

$$\begin{aligned}
|S_{00}\rangle &= 2^{-1/2}(|\alpha\beta\rangle - |\beta\alpha\rangle), & |T_{1+1}\rangle &= |\alpha\alpha\rangle, \\
|T_{10}\rangle &= 2^{-1/2}(|\alpha\beta\rangle + |\beta\alpha\rangle), & |T_{1-1}\rangle &= |\beta\beta\rangle.
\end{aligned} \tag{59}$$

These states have definite permutation symmetry under the spin permutation P_{12}

$$P_{12}|S_{00}\rangle = -|S_{00}\rangle, \quad P_{12}|T_{1m}\rangle = +|T_{1m}\rangle, \tag{60}$$

with the singlet state being anti-symmetric and the triplet-state being symmetric. The same information is encoded by the Schur-Weyl duality theorem. According to equation 58 it is only necessary to consider integer partitions with $l(\lambda) \leq 2$. For two particles the possible partition are given by

$$\lambda \vdash 2 = \{[2], [11]\}. \tag{61}$$

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The branching rule for the SO(3) $\subset U(2)$ subgroup chain follows the simple rule $I = \frac{1}{2}(\lambda_1 - \lambda_2)$[45,76]

$$I = \frac{1}{2}(2 - 0) = 1 \leftrightarrow [2], \quad I = \frac{1}{2}(1 - 1) = 0 \leftrightarrow [11]. \tag{62}$$

This leads to the following dual pairing of irreducible representations of SO(3) $\subset U(2)$ and S_2

$$\mathbb{H} = D^1 \circ D^{[2]} \oplus D^0 \circ D^{[11]}. \tag{63}$$

Equation 63 agrees with equations 59 and 60 if we identify $[2]$ with the symmetric and $[11]$ with the anti-symmetric irreducible representation of S_2. And as indicated in table IV, the multiplicities and dimensionalities follow the pattern $m_{\{\lambda\}} = d_{[\lambda]}$ and vice versa.

Γ_j	m_{Γ_j}	d_{Γ_j}
$I=1$	1	3
$\lambda = [2]$	3	1
$I=0$	1	1
$\lambda = [11]$	1	1

Table IV. Dimensionality and multiplicity pairing for SO(3) $\subset U(2)$ and S_2.

Similarly for three identical spin-1/2 particles the following partitions are of relevance

$$\lambda \vdash 3 = \{[3], [21]\}. \tag{64}$$

Repeating the argument above one may decompose $\mathbb{H}$ as follows

$$\mathbb{H} = D^{\frac{3}{2}} \circ D^{[3]} \oplus D^{\frac{1}{2}} \circ D^{[21]}. \tag{65}$$

The Schur-Weyl duality thus explains the absence of the $[111]$ or A_2 irreducible representation of S_3 for the coupling of three spin-1/2 particles[14–17,59]. With the help of the S_3 character table (see table II) it is straightforward to construct the dimensionality and multiplicity pairings as shown in table V.

For systems with $I > 1/2$ the branching rules for the SO(3) $\subset U(2I+1)$ subgroup chain are not unique. In these cases the branching rules can be built up recursively based on ideas by Jahn[76].

Γ_j	m_{Γ_j}	d_{Γ_j}
$I=\frac{3}{2}$	1	4
$\lambda = [3]$	4	1
$I=\frac{1}{2}$	2	2
$\lambda = [21]$	2	2

Table V. Dimensionality and multiplicity pairing for $\mathrm{SO}(3) \subset U(2)$ and S_3.

We illustrate the Schur-Weyl duality for spins with $I > 1/2$ by considering three coupled spin-1 particles. Such systems are interesting in the context of long-lived spin operators for deuterated methyl rotors[18,77]. For spin-1 particles it is necessary to consider partitions up to length three:

$$\lambda \vdash 3 = \{[3], [21], [111]\}. \tag{66}$$

The dual pairings for $\mathrm{SO}(3) \subset U(3)$ are given by the relations below

$$\mathbb{H} = (D^1 \oplus D^3) \circ D^{[3]} \oplus (D^1 \oplus D^2) \circ D^{[21]} \oplus D^0 \circ D^{[111]}. \tag{67}$$

Since the irreducible representations from $U(3)$ do not remain irreducible upon restriction to $\mathrm{SO}(3)$ the dual-pairings between $\mathrm{SO}(3) \subset U(3)$ and S_3 are not unique.

The multiplicities of the irreducible representations may be determined by realising that every individual pairing has to fulfill the multiplicity-dimensionality pattern. This leads to a simple set of rules.

- (1) Distribute the dual-pairing over all direct sums.

- (2) Multiply the SO(3) irreducible representation by the dimensionality of the S_n irreducible representation and vice versa.

For the current example this reduces to the following sequence of steps:

$$\begin{aligned}
&(D^1 \oplus D^3) \circ D^{[3]} \oplus (D^1 \oplus D^2) \circ D^{[21]} \oplus D^0 \circ D^{[111]} \\
&\overset{(1)}{=} D^1 \circ D^{[3]} \oplus D^1 \circ D^{[3]} \oplus D^1 \circ D^{[21]} \oplus D^2 \circ D^{[21]} \oplus D^0 \circ D^{111} \\
&\overset{(2)}{=} (D^1 \circ 3 \times D^{[3]}) \oplus (D^3 \circ 7 \times D^{[3]}) \oplus (2 \times D^1 \circ 3 \times D^{[21]}) \\
&\oplus (2 \times D^2 \circ 5 \times D^{[21]}) \oplus (D^0 \circ D^{[111]}).
\end{aligned} \tag{68}$$

The last line of equation 68 has been summarised in table III D to illustrate the individual dual-pairings.

Γ_j	m_{Γ_j}	d_{Γ_j}	Γ_j	m_{Γ_j}	d_{Γ_j}
$I=0$	1	1	$I=2$	2	5
$\lambda = [111]$	1	1	$\lambda = [21]$	5	2
$I=1$	1	3	$I=3$	1	7
$\lambda = [3]$	3	1	$\lambda = [3]$	7	1
$I=1$	2	3			
$\lambda = [21]$	3	2			

Table VI. Dimensionality and multiplicity pairing for $SO(3) \subset U(3)$ and S_3.

While it is straightforward to determine the dimensionality of an irreducible representation D^I, it is not straightforward to calculate the dimensionality of an irreducible representation $D^{[\lambda]}$. Since the following discussion will focus on spin systems with $I = 1/2$ and $I = 1$ we provide expressions for the dimensionality of $D^{[\lambda]}$ with $l(\lambda) \leq 3$

$$
\begin{aligned}
d_{\lambda,1}(\lambda_1) &= 1, \\
d_{\lambda,2}(\lambda_1, \lambda_2) &= (\lambda_1 + \lambda_2)! \frac{(\lambda_1 - \lambda_2 + 1)}{(\lambda_1 + 1)! \lambda_2!}, \\
d_{\lambda,3}(\lambda_1, \lambda_2, \lambda_3) &= \\
(\lambda_1 + \lambda_2 + \lambda_3)! &\frac{(\lambda_1 - \lambda_2 + 1)(\lambda_1 - \lambda_3 + 1)(\lambda_2 - \lambda_3 + 2)}{(\lambda_1 + 2)!(\lambda_2 + 1)! \lambda_3!}.
\end{aligned}
\tag{69}
$$

A derivation of these is given in appendix A 1.

E. Long-lived spin operators

1. Permutational symmetry

Long-lived spin populations and long-lived spin coherences possess exceptional relaxation time constants. This indicates that they are either exact or approximate members of the nullspace of $\hat{\mathcal{R}}$ (strictly speaking one should consider the nullspace of $\hat{\mathcal{L}}_{coh} + \hat{\mathcal{R}}$, but this distinction will be inconsequential for the following discussion)[48]. The elements of

the nullspace $\mathrm{Null}(\hat{\mathcal{R}})$ may be constructed by imposing symmetries on $\hat{\mathcal{R}}$. Practically this is achieved by synthesising molecules with a high degree of local symmetry and rigid molecular structure[78–80].

In the NMR literature it is often assumed that long-lived spin operators are encountered if $\hat{\mathcal{R}}$ is invariant under the permutation group of $\mathcal{H}_{\mathrm{coh}}$ (or one of its subgroups)[14–16]. But this conclusion is incorrect. The relaxation superoperator has to obey a stricter symmetry principle. For long-lived spin operators to exist $\hat{\mathcal{R}}$ has to be invariant under the following direct product group

$$\mathrm{S}_n^2 = \mathrm{S}_n \otimes \mathrm{S}_n^*. \tag{70}$$

The elements of S_n^2 are given by generalised spin permutation superoperators $\hat{P}_\sigma^\tau$

$$\hat{P}_\sigma^\tau = P_\sigma \otimes P_\tau^* \quad \text{with} \quad \sigma, \tau \in \mathrm{S}_n. \tag{71}$$

These operate on $\mathbb{H}$ and its dual $\mathbb{H}^*$, respectively.

To see why $\hat{\mathcal{R}}$ has to be invariant under S_n^2, we first consider a system without any symmetry. In this case the only member of $\mathrm{Null}(\hat{\mathcal{R}})$ is the sum of all populations $|\mathbb{1})$

$$\hat{\mathcal{R}}|\mathbb{1}) = |\mathbb{0}). \tag{72}$$

The identity operator may be decomposed by making use of the projectors $\mathcal{P}^{[\lambda]}$ onto the different symmetry manifolds of S_n on $\mathbb{H}$[44–47]

$$\mathcal{P}^{[\lambda]} = \frac{d_{[\lambda]}}{|\mathrm{S}_n|} \sum_{\sigma \in \mathrm{S}_n} (\chi^{[\lambda]}(\sigma))^* P_\sigma. \tag{73}$$

Equation 72 may then be expressed as shown below

$$\hat{\mathcal{R}}|\mathbb{1}) = \sum_{\lambda \vdash n} \hat{\mathcal{R}}|\mathcal{P}^{[\lambda]} \mathbb{1} \mathcal{P}^{[\lambda],\dagger}) = \sum_{\lambda \vdash n} \hat{\mathcal{R}}\hat{\mathcal{P}}^{[\lambda]}|\mathbb{1}), \tag{74}$$

where we have defined the following projection superoperator

$$\hat{\mathcal{P}}^{[\lambda]} = \mathcal{P}^{[\lambda]} \otimes \mathcal{P}^{[\lambda],*}. \tag{75}$$

Assuming that $\hat{\mathcal{R}}$ commutes with every projector $\hat{\mathcal{P}}^{[\lambda]}$ equation 74 reduces to the following

$$\hat{\mathcal{R}}|\mathbb{1}) = \sum_{\lambda \vdash n} \hat{\mathcal{P}}^{[\lambda]}\hat{\mathcal{R}}|\mathbb{1}) = |\mathbb{0}). \tag{76}$$

The projectors $\hat{\mathcal{P}}^{[\lambda]}$ however may not be constructed from the set

$$\{\hat{P}^\sigma_\sigma\} = \{\hat{P}_\sigma\} \quad \sigma \in S_n, \tag{77}$$

which generates a representation of S_n on $\mathbb{L}(\mathbb{H})$. Instead they are constructed from the elements of the group S_n^2. This implies that $\hat{\mathcal{R}}$ has to be at least S_n^2 symmetric.

The physical interpretation for this is straightforward. Consider for example a system dominated by dipolar relaxation. The dipolar relaxation superoperator may be expressed as follows[61,62]:

$$\hat{\mathcal{R}} = \hat{\mathcal{R}}^+ + \hat{\mathcal{R}}^\times,$$

$$\hat{\mathcal{R}}^+ = \sum_{i<j}^N \sum_{m=-2}^{+2} (-1)^m b_{2m}^{(ij,ij)} \hat{T}_{2m}^{ij} \hat{T}_{2-m}^{ij},$$

$$\hat{\mathcal{R}}^\times = \sum_{i<j,p<q}^N (1 - \delta_{ip}\delta_{jq}) \sum_{m=-2}^{+2} (-1)^m b_{2m}^{(ij,pq)} \hat{T}_{2m}^{ij} \hat{T}_{2-m}^{pq}, \tag{78}$$

with $\hat{\mathcal{R}}^+$ being auto-correlation terms and $\hat{\mathcal{R}}^\times$ being cross-correlation terms. The commutation superoperators $\hat{T}_{2m}^{ij}$ are constructed by coupling rank one ISTO of spins i and j into a rank two ISTO. The relaxation rate constants $b_{2m}^{(ij,pq)}$ may be derived from the molecular geometry of the molecule[61,62]. The action of a generalised permutation superoperator $\hat{P}^\tau_\sigma$ onto $\hat{\mathcal{R}}$ is given by conjugation

$$\hat{P}^\tau_\sigma : \hat{\mathcal{R}} \mapsto \hat{P}^\tau_\sigma \hat{\mathcal{R}} \hat{P}^{\tau,\dagger}_\sigma. \tag{79}$$

Instead of acting onto the superoperators the permutations may alternatively act on the relaxation rate constants

$$\hat{P}^\tau_\sigma : b_{2m}^{(ij,pq)} \mapsto b_{2m}^{(\sigma(i)\sigma(j),\tau(p)\tau(q))}. \tag{80}$$

This way it is easy to see that S_n operations on $\mathbb{L}(\mathbb{H})$ permute auto-correlation terms and cross-correlation terms, but never mix auto- and cross-correlation terms for mixed m. S_n symmetry therefore describes the symmetry of $\hat{\mathcal{R}}^+$ and $\hat{\mathcal{R}}^\times$ separately. For exact long-lived spin operators to exist however, it is necessary that $\hat{\mathcal{R}}$ remains invariant even if auto- and cross-correlation terms are exchanged. Such symmetries are described by S_n^2 and not by S_n.

Making use of the considerations above we have the following result regarding the nullspace of a relaxation superoperator $\hat{\mathcal{R}}$.

Theorem III.1. *The nullspace* $\mathrm{Null}(\hat{\mathcal{R}}^{S_n^2})$ *of an* S_n^2 *symmetric relaxation superoperator* $\hat{\mathcal{R}}^{S_n^2}$ *is given by the set of generalised group projection operators* $\mathcal{P}^{[\lambda]}_{\gamma\delta}$

$$\mathrm{Null}(\hat{\mathcal{R}}^{S_n^2}) = \{|\mathcal{P}^{[\lambda]}_{\gamma\delta})\}. \tag{81}$$

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Proof. Let $[\lambda]$ be an irreducible representation of S_n. A group projection operator $\mathcal{P}_{\gamma\delta}^{[\lambda]}$ onto the $[\lambda]$-subspace is defined as follows[44–47]

$$\mathcal{P}_{\gamma\delta}^{[\lambda]} = \frac{d_{[\lambda]}}{|S_n|} \sum_{\sigma \in S_n} [D^{[\lambda]}(\sigma)]_{\gamma\delta}^* P_\sigma. \tag{82}$$

If considered as states in $\mathbb{L}(\mathbb{H})$ the action of $\hat{\mathcal{R}}^{S_n^2}$ onto $|\mathcal{P}_{\gamma\delta}^{[\lambda]})$ may be expressed as follows

$$\begin{aligned}
\hat{\mathcal{R}}^{S_n^2}|\mathcal{P}_{\gamma\delta}^{[\lambda]}) &= \frac{d_{[\lambda]}}{|S_n|} \sum_{\sigma \in S_n} [D^{[\lambda]}(\sigma)]_{\gamma\delta}^* \hat{\mathcal{R}}^{S_n^2}(P_\sigma \otimes \mathbb{1})|\mathbb{1}) \\
\hat{\mathcal{R}}^{S_n^2}|\mathcal{P}_{\gamma\delta}^{[\lambda]}) &= \frac{d_{[\lambda]}}{|S_n|} \sum_{\sigma \in S_n} [D^{[\lambda]}(\sigma)]_{\gamma\delta}^* (P_\sigma \otimes \mathbb{1})\hat{\mathcal{R}}^{S_n^2}|\mathbb{1}) = |\mathbb{0}),
\end{aligned} \tag{83}$$

where the second line is a result of the S_n^2 symmetry of $\hat{\mathcal{R}}^{S_n^2}$. The set of group projectors $|\mathcal{P}_{\gamma\delta}^{[\lambda]})$ therefore spans the nullspace of $\hat{\mathcal{R}}^{S_n^2}$

$$\text{Null}(\hat{\mathcal{R}}^{S_n^2}) = \{|\mathcal{P}_{\gamma\delta}^{[\lambda]})\}. \tag{84}$$

$\square$

A bound on the number of long-lived spin operators may be determined by expressing the $\mathcal{P}_{\gamma\delta}^{[\lambda]}$ in terms of the symmetry adapted basis states $\mathcal{B}^{S_n}$

$$\mathcal{P}_{\gamma\delta}^{[\lambda]} = \sum_{\mu=1}^{m_{[\lambda]}} |[\lambda], \gamma, \mu\rangle\langle[\lambda], \delta, \mu|. \tag{85}$$

The number of long-lived spin operators is then bounded by the following relations:

Corollary III.1.1. *For a S_n^2 symmetric relaxation superoperator $\hat{\mathcal{R}}^{S_n^2}$ the number of long-lived spin populations N_{LLS}^P is bounded by*

$$N_{LLS}^P \geq \sum_{j=1}^{N_\Gamma} d_{\Gamma_j}. \tag{86}$$

Corollary III.1.2. *For a S_n^2 symmetric relaxation superoperator $\hat{\mathcal{R}}^{S_n^2}$ the number of long-lived spin coherences N_{LLS}^C is bounded by*

$$N_{LLS}^C \geq \sum_{j=1}^{N_\Gamma} d_{\Gamma_j}^2 - d_{\Gamma_j}. \tag{87}$$

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Corollaries III.1.1 and III.1.2 implicitly assume that the summations are carried out over the set of irreducible representations supported by $\mathbb{H}$. Without presence of any further symmetries one may invoke the equal signs. However, as shown in section III F dual-selection rules including rotational and permutational symmetries may lead to an increased number of long-lived spin operators.

Assuming no further symmetries for the moment, the upper bounds given by corollaries III.1.1 and III.1.2 resolve the apparent paradox presented in the introduction. According to the bounds given in reference 16 the number of long-lived populations bounded by A_3 and S_3 symmetry are $N^P_{LLS} = 3$ and $N^P_{LLS} = 2$, respectively. By taking the dimensionality of the irreducible representations into account both groups A_3 and S_3 lead to identical results, namely $N^P_{LLS} = 3$.

This may be seen as follows. The coherent Hamiltonian for a methyl-rotor is S_3 and A_3 symmetric. Since A_3 is a subgroup of S_3 it is always possible to choose a symmetry adapted basis that remains irreducible for the subgroup chain $A_3 \subset S_3$. In table VII we have listed the branching rules for the $A_3 \subset S_3$ subgroup chain. Upon restriction from S_3 to A_3 the two-dimensional E subspace splits into two one-dimensional subspaces E_a and E_b. As a consequence the overall number of long-lived populations remains constant.

Γ_j	A	E_a	E_b
A_1	1	0	0
A_2	1	0	0
E	0	1	1

Table VII. Branching rules for the irreducible representations of S_3 upon restriction to A_3. The irreducible representations have been labelled according to the crystallographic point group convention.

Consider now the number of long-lived spin coherences. It is clear that the prediction of long-lived coherences differs for the groups S_3 and A_3. For the group S_3 one finds $N^C_{LLS} = 2$ since the irreducible representation E is two-dimensional. But for the group A_3 one finds $N^C_{LLS} = 0$. This simple example shows that the bigger group, S_3 in this case, carries more information than A_3, so that in general one should always use the maximal symmetry group

of the relaxation superoperator $\hat{\mathcal{R}}$.

Besides the existence of long-lived spin operators, the S_n^2 symmetry imposes a block structure onto the matrix representation of $\hat{\mathcal{R}}^{\mathrm{S}_n^2}$ when expressed in the outer tensor basis of symmetry adapted basis states $\mathcal{B}^{\mathrm{S}_n}$

$$\hat{\mathcal{B}}^{\mathrm{S}_n^2} = \{|[\lambda], \gamma, \mu; [\kappa], \delta, \nu)\} = \mathcal{B}^{\mathrm{S}_n} \otimes \mathcal{B}^{\mathrm{S}_n^*}, \tag{88}$$

where we have introduced the following short-hand notation

$$||[\lambda], \gamma, \mu\rangle\langle[\kappa], \delta, \nu|) = |[\lambda], \gamma, \mu; [\kappa], \delta, \nu). \tag{89}$$

A general matrix element of $\hat{\mathcal{R}}^{\mathrm{S}_n^2}$ may then be expressed as follows

$$([\lambda'], \gamma', \mu'; [\kappa'], \delta', \nu'|\hat{\mathcal{R}}^{\mathrm{S}_n^2}|[\lambda], \gamma, \mu; [\kappa], \delta, \nu). \tag{90}$$

Due to S_n^2 symmetry we may replace $\hat{\mathcal{R}}^{\mathrm{S}_n^2}$ by $\hat{P}_\sigma^{e,\dagger}\hat{\mathcal{R}}^{\mathrm{S}_n^2}\hat{P}_\sigma^e$ and sum over $\sigma \in \mathrm{S}_n$

$$
\begin{aligned}
&\sum_{\sigma \in \mathrm{S}_n} ([\lambda'], \gamma', \mu'; [\kappa'], \delta', \nu'|\hat{P}_\sigma^{e,\dagger}\hat{\mathcal{R}}^{\mathrm{S}_n^2}\hat{P}_\sigma^e|[\lambda], \gamma, \mu; [\kappa], \delta, \nu) = \\
&\sum_{\sigma \in \mathrm{S}_n} (P_\sigma([\lambda'], \gamma', \mu'); [\kappa'], \delta', \nu'|\hat{\mathcal{R}}^{\mathrm{S}_n^2}|P_\sigma([\lambda], \gamma, \mu); [\kappa], \delta, \nu) = \\
&\sum_{\alpha, \alpha'} \sum_{\sigma \in \mathrm{S}_n} ([\lambda'], \alpha', \mu'; [\kappa'], \delta', \nu'|\hat{\mathcal{R}}^{\mathrm{S}_n^2}|[\lambda], \alpha, \mu; [\kappa], \delta, \nu) \times [D^{[\lambda]}(\sigma)]_{\alpha\gamma}[D^{[\lambda']}(\sigma)]_{\alpha'\gamma'}^*.
\end{aligned} \tag{91}
$$

The last line may be simplified by making use of the Schur-orthogonality relations (see equation 23)

$$
\begin{aligned}
&([\lambda'], \gamma', \mu'; [\kappa'], \delta', \nu'|\hat{\mathcal{R}}^{\mathrm{S}_n^2}|[\lambda], \gamma, \mu; [\kappa], \delta, \nu) = \\
&\frac{|\mathrm{S}_n|}{d_{[\lambda]}} \sum_\alpha ([\lambda'], \alpha, \mu'; [\kappa'], \delta', \nu'|\hat{\mathcal{R}}^{\mathrm{S}_n^2}|[\lambda], \alpha, \mu; [\kappa], \delta, \nu) \times \delta_{[\lambda'][\lambda]}\delta_{\gamma'\gamma}.
\end{aligned} \tag{92}
$$

In a second step one may replace $\hat{\mathcal{R}}^{\mathrm{S}_n^2}$ by $\hat{P}_e^{\sigma,\dagger}\hat{\mathcal{R}}^{\mathrm{S}_n^2}\hat{P}_e^\sigma$ and perform the same steps again. A generic matrix element is then constrained by the following relation:

$$([\lambda'], \gamma', \mu'; [\kappa'], \delta', \nu'|\hat{\mathcal{R}}^{\mathrm{S}_n^2}|[\lambda], \gamma, \mu; [\kappa], \delta, \nu) \propto \delta_{[\lambda'][\lambda]}\delta_{[\kappa'][\kappa]}\delta_{\gamma'\gamma}\delta_{\delta'\delta}. \tag{93}$$

This indicates that $\hat{\mathcal{R}}^{\mathrm{S}_n^2}$ may not mix either of the permutation symmetries of the operators $|[\lambda], \gamma, \mu\rangle\langle[\kappa], \delta, \nu|$ and its matrix representation splits up into the blocks $([\lambda][\kappa], [\lambda][\kappa])$. The block $([\lambda][\kappa], [\lambda][\kappa])$ is additionally split into $(d_{[\lambda]} \times d_{[\kappa]})$ blocks since the group projection numbers γ and δ have to match.

For the case of three-identical spin-1/2 particles the relaxation matrix of $\hat{\mathcal{R}}^{S^2_n}$ takes the following form for example

$$
\hat{\mathcal{R}}^{S^2_n} =
\begin{bmatrix}
 & [3][3] & [21][21] & [3][21] & [21][3] \\
\hline
[3][3] & \blacksquare & 0 & 0 & 0 \\
[21][21] & 0 & \blacksquare & 0 & 0 \\
[3][21] & 0 & 0 & \blacksquare & 0 \\
[21][3] & 0 & 0 & 0 & \blacksquare
\end{bmatrix}.
\tag{94}
$$

F. Rotational symmetries

So far we have only considered permutational symmetries of the relaxation superoperator. We will continue assuming that $\hat{\mathcal{R}}$ is S^2_n symmetric but additionally consider rotational symmetries.

The treatment of rotational symmetries for a relaxation superoperator requires some care. In principal $\hat{\mathcal{R}}^{S^2_n}$ may possess "two types" of rotational symmetry. To see this a generic S^2_n symmetric relaxation superoperator $\hat{\mathcal{R}}^{S^2_n}$ originating from rotational diffusion processes (neglecting cross-relaxation terms) is expanded as follows[61,62]

$$
\hat{\mathcal{R}}^{S^2_n} = \sum_{k=1}^{2} \sum_{m=-k}^{+k} a_{km} \sum_{i,p}^{N} \hat{A}^{i}_{km} \hat{A}^{p,\dagger}_{km} + \sum_{k=1}^{2} \sum_{m=-k}^{+k} b_{km} \sum_{i<j,p<q}^{N} \hat{B}^{ij}_{km} \hat{B}^{pq,\dagger}_{km},
\tag{95}
$$

where the superoperators $\hat{A}$ are derived from linear and the superoperators $\hat{B}$ from bilinear spin operators[61,62]. S^2_n permutation symmetry implies that the relaxation rate constants a_{km} and b_{km} are independent of (i,j,p,q) for fixed (k,m). This enables the definition of effective commutation superoperators as shown below

$$
\sum_{i} \hat{A}^{i}_{km} = \hat{A}^{[N]}_{km} \quad \text{and} \quad \sum_{i<j} \hat{B}^{ij}_{km} = \hat{B}^{[N]}_{km}.
\tag{96}
$$

The notation $\hat{A}^{[N]}$ and $\hat{B}^{[N]}$ reflects the fact that these superoperators are invariant under elements of S_n. The relaxation superoperator in equation 95 is then replaced by the following

$$
\hat{\mathcal{R}}^{S^2_n} = \sum_{k=1}^{2} \sum_{m=-k}^{+k} a_{km} \hat{A}^{[N]}_{km} \hat{A}^{[N],\dagger}_{km} + \sum_{k=1}^{2} \sum_{m=-k}^{+k} b_{km} \hat{B}^{[N]}_{km} \hat{B}^{[N],\dagger}_{km}.
\tag{97}
$$

The first type of rotational symmetry implies that $\hat{\mathcal{R}}^{S^2_n}$ is invariant under rotations in $\mathbb{L}(\mathbb{H})$. These type of rotations are generated by the commutation superoperators of the

Cartesian angular momentum operators. The superoperator equivalent of equation 11 is then

$$\hat{R}(\alpha, \beta, \gamma) = \hat{R}_z(\alpha)\hat{R}_y(\beta)\hat{R}_z(\gamma) = \exp\left\{-i\alpha\hat{I}_z\right\}\exp\left\{-i\beta\hat{I}_y\right\}\exp\left\{-i\gamma\hat{I}_z\right\}. \tag{98}$$

For the relaxation superoperator of equation 97 this means that relaxation rate constants a_{km} and b_{km} are independent of m

$$\hat{\mathcal{R}}_{SO(3)}^{S_n^2} = \sum_{k=1}^{2} a_k \sum_{m=-k}^{+k} \hat{A}_{km}^{[N]}\hat{A}_{km}^{[N],\dagger} + \sum_{k=1}^{2} b_k \sum_{m=-k}^{+k} \hat{B}_{km}^{[N]}\hat{B}_{km}^{[N],\dagger}. \tag{99}$$

This is often the case for relaxation in the fast motion limit, but we will not make this assumption here[61,62,64,65].

The second type of rotational symmetry is inherited from $\mathbb{H}$. This may be seen by evaluation of an arbitrary matrix element of $\hat{\mathcal{R}}^{S_n^2}$. For simplicity we consider the bilinear term as the argument easily generalises to linear terms. A matrix element for fixed (k, m) may be calculated as shown below

$$(a; b|\hat{B}_{km}^{[N]}\hat{B}_{km}^{[N],\dagger}|c; d) = \text{Tr}\{(|a\rangle\langle b|)^{\dagger}[B_{km}^{[N]}, [B_{km}^{[N],\dagger}, |c\rangle\langle d|]]\}. \tag{100}$$

Evaluation of the trace results in the following

$$\begin{aligned}(a; b|\hat{B}_{km}^{[N]}\hat{B}_{km}^{[N],\dagger}|c; d) =& \langle a|B_{km}^{[N]}B_{km}^{[N],\dagger}|c\rangle \langle b|d\rangle + \langle d|B_{km}^{[N],\dagger}B_{km}^{[N]}|b\rangle \langle a|c\rangle \\ &- \langle a|B_{km}^{[N]}|c\rangle\langle d|B_{km}^{[N],\dagger}|b\rangle - \langle a|B_{km}^{[N],\dagger}|c\rangle\langle d|B_{km}^{[N]}|b\rangle.\end{aligned} \tag{101}$$

So far the states $|a\rangle$, $|b\rangle$, $|c\rangle$ and $|d\rangle$ have been arbitrary. Consider replacing these by total angular momentum states $|I_1\rangle$, $|I_2\rangle$, $|I_3\rangle$ and $|I_4\rangle$. Since all quantities involved possess definite total angular momentum the expectation values of equation 101 are subjected to the Wigner-Eckart-theorem[44–47]. But by virtue of the Schur-Weyl duality theorem one may always find total angular momentum states $|I\rangle$ that transform irreducibly under S_n and SO(3) simultaneously. These states form a dual-basis for S_n and SO(3)

$$\mathcal{B}_{SO(3)}^{S_n} = \{|[\lambda], I\rangle\}. \tag{102}$$

In this case the matrix elements of equation 101 obey dual-selection rules reflecting their rotational and permutational symmetry.

Dual-selection rules may be derived by introducing dual-basis states into equation 101. The first contribution is subjected to the following selection rules

$$
\begin{aligned}
&\langle [\lambda], I_1 | B_{km}^{[N]} B_{km}^{[N],\dagger} | [\lambda'], I_3 \rangle \langle [\kappa], I_2 | [\kappa'], I_4 \rangle = \\
&\sum_{j \in [\lambda]} \langle [\lambda], I_1 | B_{km}^{[N]} | [\lambda], j \rangle \langle [\lambda], j | B_{km}^{[N],\dagger} | [\lambda'], I_3 \rangle \langle [\kappa], I_2 | [\kappa'], I_4 \rangle \propto \\
&\sum_{j \in [\lambda]} \delta_{[\lambda][\lambda']} \delta_{[\kappa][\kappa']} \delta_{I_2 I_4} \Delta(I_1, k, j) \Delta(I_3, k, j)
\end{aligned}
\tag{103}
$$

and similarly for the second contribution:

$$
\begin{aligned}
&\langle [\kappa'], I_4 | B_{km}^{[N],\dagger} B_{km}^{[N]} | [\kappa], I_2 \rangle \langle [\lambda], I_1 | [\lambda'], I_3 \rangle = \\
&\sum_{j \in [\kappa]} \langle [\kappa'], I_4 | B_{km}^{[N],\dagger} | [\kappa], j \rangle \langle [\kappa], j | B_{km}^{[N]} | [\kappa], I_2 \rangle \langle [\lambda], I_1 | [\lambda'], I_3 \rangle \propto \\
&\sum_{j \in [\kappa]} \delta_{[\lambda][\lambda']} \delta_{[\kappa][\kappa']} \delta_{I_1 I_3} \Delta(I_2, k, j) \Delta(I_4, k, j),
\end{aligned}
\tag{104}
$$

where j runs over all total angular momentum values that may pair up with the irreducible representation $D^{[\lambda]}$ or $D^{[\kappa]}$. The symbol $\Delta(j_1, j_2, j_3)$ describes the triangular conditions the angular momenta have to satisfy. It has the following properties[4,5,44–47]

$$
\Delta(j_1, j_2, j_3) = \begin{cases} 1 & \text{for } j_3 \in \{|j_1 - j_2|, |j_1 - j_2| + 1, \ldots, |j_1 + j_2|\} \\ 0 & \text{for } j_3 \notin \{|j_1 - j_2|, |j_1 - j_2| + 1, \ldots, |j_1 + j_2|\} \end{cases} .
\tag{105}
$$

The third and fourth contributions to the matrix elements of $\hat{\mathcal{R}}^{\mathrm{S}_n^2}$ are significantly simpler and are constrained by the same selection rules

$$
\begin{aligned}
&\langle [\lambda], I_1 | B_{km}^{[N]} | [\lambda'], I_3 \rangle \langle [\kappa'], I_4 | B_{km}^{[N],\dagger} | [\kappa], I_2 \rangle \propto \delta_{[\lambda][\lambda']} \delta_{[\kappa][\kappa']} \Delta(I_1, k, I_3) \Delta(I_2, k, I_4) \\
&\langle [\lambda], I_1 | B_{km}^{[N],\dagger} | [\lambda'], I_3 \rangle \langle [\kappa'], I_4 | B_{km}^{[N]} | [\kappa], I_2 \rangle \propto \delta_{[\lambda][\lambda']} \delta_{[\kappa][\kappa']} \Delta(I_1, k, I_3) \Delta(I_2, k, I_4).
\end{aligned}
\tag{106}
$$

Collecting all selection rules from equations 103, 104 and 106 leads to rotational and permutational dual-selection rules for the relaxation superoperator $\hat{\mathcal{R}}^{\mathrm{S}_n^2}$ for fixed k and m

$$
\begin{aligned}
&([\lambda] I_1; [\kappa] I_2 | \hat{\mathcal{R}}^{\mathrm{S}_n^2} | [\lambda'] I_3; [\kappa'] I_4) \propto \delta_{[\lambda'][\lambda]} \delta_{[\kappa'][\kappa]} \delta_{\gamma' \gamma} \delta_{\delta' \delta} \\
&\left(\sum_{j \in [\lambda]} \delta_{I_2 I_4} \Delta(I_1, k, j) \Delta(I_3, k, j) + \sum_{j \in [\kappa]} \delta_{I_1 I_3} \Delta(I_2, k, j) \Delta(I_4, k, j) - \Delta(I_1, k, I_3) \Delta(I_2, k, I_4) \right),
\end{aligned}
\tag{107}
$$

where we have made us of equation 93 to introduce the missing group selection rules.

The selection rules of equation 107 are readily generalised for the case that $\hat{\mathcal{R}}^{S_n^2}_{SO(3)}$ is invariant under permutations and rotations in $\mathbb{L}(\mathbb{H})$. Since the relaxation rate constants for $\hat{\mathcal{R}}^{S_n^2}_{SO(3)}$ are independent of m one may simply sum equation 107 over m for fixed k

$$([\lambda]I_1; [\kappa]I_2|\hat{\mathcal{R}}^{S_n^2}_{SO(3)}|[\lambda']I_3; [\kappa']I_4) = \sum_{m=-k}^{+k} ([\lambda]I_1; [\kappa]I_2|\hat{\mathcal{R}}^{S_n^2}|[\lambda']I_3; [\kappa']I_4) \propto$$
$$\delta_{[\lambda'][\lambda]}\delta_{[\kappa'][\kappa]}\delta_{\gamma'\gamma}\delta_{\delta'\delta}\left(\delta_{I_1 I_3}\delta_{I_2 I_4}\left(\sum_{j\in[\lambda]}\Delta(I_1,k,j) + \sum_{j\in[\kappa]}\Delta(I_2,k,j)\right) - \Delta(I_1,k,I_3)\Delta(I_2,k,I_4)\right).$$
$$(108)$$

When expressed in the outer tensor product basis of dual-symmetry adapted basis states $\mathcal{B}^{S_n}_{SO(3)}$ the dual-selection rules in equation 107 and 108 indicate that the relaxation super-operators $\hat{\mathcal{R}}^{S_n^2}$ or $\hat{\mathcal{R}}^{S_n^2}_{SO(3)}$ take on the general block structure $([\lambda][\kappa], [\lambda][\kappa])$ as discussed in section III C. Additionally, within each symmetry block $([\lambda][\kappa], [\lambda][\kappa])$ the elements are subjected to triangular conditions that may lead to an increase in the number of long-lived spin operators. Examples of such cases are discussed in the next sections. In particular we will consider spin-1/2 and spin-1 systems which are commonly encountered in the context of long-lived spin order[14–18,24,25].

IV. SYSTEMS OF SPIN-1/2 PARTICLES

Consider the dual-selection rules of equation 107 for spin-1/2 systems. Since the dual-pairings for S_n and $SO(3) \subset U(2)$ irreducible representations are unique it is permissible to replace I_3 with I_1 and I_4 with I_2 under the Kronecker deltas $\delta_{[\lambda][\lambda']}$ and $\delta_{[\kappa][\kappa']}$

$$([\lambda]I_1; [\kappa]I_2|\hat{\mathcal{R}}^{S_n^2}|[\lambda']I_3; [\kappa']I_4) \propto$$
$$\delta_{[\lambda][\lambda']}\delta_{[\kappa][\kappa']}\left(\sum_{j\in[\lambda]}\Delta(I_1,k,j) + \sum_{j\in[\kappa]}\Delta(I_2,k,j) - \Delta(I_1,k,I_1)\Delta(I_2,k,I_2)\right).$$
$$(109)$$

One may further replace I_1 and I_2 by the corresponding partitions $[\lambda]$ and $[\kappa]$. This way one may eliminate the summations by virtue of uniqueness of the dual-pairing. This leads to the simplified dual-selection rules for spin-1/2 systems as indicated below

$$([\lambda]I_1; [\kappa]I_2|\hat{\mathcal{R}}^{S_n^2}|[\lambda']I_3; [\kappa']I_4) \propto$$
$$\delta_{[\lambda][\lambda']}\delta_{[\kappa][\kappa']}\left(\Delta([\lambda],k,[\lambda]) + \Delta([\kappa],k,[\kappa]) - \Delta([\lambda],k,[\lambda])\Delta([\kappa],k,[\kappa])\right).$$
$$(110)$$

For spin-1/2 systems it is therefore sufficient to consider diagonal triangular conditions.

To analyse the implications of such dual-selection rules it is advantageous to treat spin-1/2 systems with an even and odd number of particles separately. As it turns out these two cases will behave differently under rotational-permutational dual-symmetry.

A. Odd number of spins

For a system of N spin-1/2 particles with N being odd the relevant integer partitions are given by

$$\lambda \in \{[N], [N-1\ 1], [N-2\ 2], \ldots, [\tfrac{1}{2}(N+1)\ \tfrac{1}{2}(N+1)-1]\}. \tag{111}$$

These pair up with the following irreducible representations of $SO(3) \subset U(2)$ (in that order)

$$I \in \{\frac{N}{2}, \frac{N}{2}-1, \ldots, \frac{1}{2}\}. \tag{112}$$

Spin operators responsible for relaxation are spherical tensors with $k = 1$ and $k = 2$, so that there is only a finite number of triangular conditions to check. It is easy to show that the following relations hold

$$\Delta(I, 1, I) = 1\ \forall I, \quad \Delta(I, 2, I) = 1\ \forall\ I > \frac{1}{2}, \quad \Delta(\frac{1}{2}, 2, \frac{1}{2}) = 0. \tag{113}$$

The triangular conditions indicate that there is no increase in the number of long-lived spin operators if relaxation mechanisms with $k \in \{1, 2\}$ are active. In this case the number of long-lived spin operators is given corollaries III.1.1 and III.1.2 with an equal sign.

The situation changes if only relaxation mechanisms with $k = 2$ are active. This applies for systems that are dominated by dipolar relaxation mechanisms. In this case the matrix elements of the subspace uniquely associated with spin angular momentum $I = 1/2$ vanish identically since all triangular conditions evaluate to zero. For three-spin-1/2 particles for example the block $([21][21], [21][21])$ vanishes completely

$$\hat{\mathcal{R}}^{S_n^2} = \begin{bmatrix} & [3][3] & [21][21] & [3][21] & [21][3] \\ \hline [3][3] & \blacksquare & 0 & 0 & 0 \\ [21][21] & 0 & 0 & 0 & 0 \\ [3][21] & 0 & 0 & \blacksquare & 0 \\ [21][3] & 0 & 0 & 0 & \blacksquare \end{bmatrix}. \tag{114}$$

30

It follows that all possible coherences and populations of the $([21][21], [21][21])$ subspace are now elements of $\mathrm{Null}(\hat{\mathcal{R}}^{\mathrm{S}_n^2})$. The total dimensionality of this block may be calculated by using the fact that $d_{1/2} = 2$ and $d_{[21]} = 2$

$$d_{[21][21]} = d_{1/2}^2 \times d_{[21]}^2 = 16. \tag{115}$$

The number of long-lived operators thus increases from $N_{\mathrm{LLS}} = 5$ to $N_{\mathrm{LLS}} = 1 + 16 = 17$, as may be verified numerically.

This idea may be generalised to any odd system of N identical spins with $I = 1/2$. As indicated by equation 112 any odd number of systems contains the representation $D^{1/2}$ and according to equation 111 the $D^{1/2}$ representation pairs with the integer partition $[\frac{1}{2}(N + 1) \, \frac{1}{2}(N + 1) - 1]$. For example for 3, 5, and 7 spins the pairings $D^{1/2} \circ D^{[21]}$, $D^{1/2} \circ D^{[32]}$, $D^{1/2} \circ D^{[43]}$ are present. The total number of long-lived spin operators may then be calculated by making use of the dimensionality function $d_{\lambda,2}$ for partitions with $l(\lambda) \le 2$ (see equation 69)

$$N_{\mathrm{LLS}} = (d_{1/2} \times d_{\lambda,2}(\tfrac{1}{2}(N + 1), \tfrac{1}{2}(N + 1) - 1))^2 + \sum_{j=0}^{\frac{1}{2}(N-3)} (d_{\lambda,2}(N - j, j))^2. \tag{116}$$

The number of long-lived spin populations and spin coherences may then be separated as indicated below

$$N_{\mathrm{LLS}}^{\mathrm{P}} = d_{1/2} \times d_{\lambda,2}(\tfrac{1}{2}(N + 1), \tfrac{1}{2}(N + 1) - 1) + \sum_{j=0}^{\frac{1}{2}(N-3)} (d_{\lambda,2}(N - j, j)),$$
$$N_{\mathrm{LLS}}^{\mathrm{C}} = N_{\mathrm{LLS}} - N_{\mathrm{LLS}}^{\mathrm{P}}. \tag{117}$$

Table VIII summarises the number of long-lived spin populations and coherences for $N \in \{3, 5, 7\}$ spins.

The group projection operators $P_{\gamma\delta}^{[\lambda]}$ which span the nullspace $\mathrm{Null}(\hat{\mathcal{R}}^{\mathrm{S}_n^2})$ are then complemented by all operators of the type

$$|[\tfrac{1}{2}(N + 1) \, \tfrac{1}{2}(N + 1) - 1], \gamma, 1/2, m_1\rangle\langle[\tfrac{1}{2}(N + 1) \, \tfrac{1}{2}(N + 1) - 1], \delta, 1/2, m_2|, \tag{118}$$

where m_1 and m_2 may take the values $+1/2$ and $-1/2$.

N	$N_{\mathrm{LLS}}^{\mathrm{P}}$	$N_{\mathrm{LLS}}^{\mathrm{C}}$	N_{LLS}
3	5	12	17
5	15	102	117
7	49	968	1017

Table VIII. The number of long-lived spin operators and spin coherences for an odd number of spin-1/2 particles experiencing relaxation mechanisms with $k = 2$.

B. Even number of spins

For a system of N spin-1/2 particles with N being even the relevant integer partitions are given by:

$$\lambda \in \{[N], [N-1\ 1], [N-2\ 2], \ldots, [N/2\ N/2]\} \tag{119}$$

These pair up with the following irreducible representations of $\mathrm{SO}(3) \subset U(2)$ (in that order):

$$I \in \{\frac{N}{2}, \frac{N}{2} - 1, \ldots, 0\} \tag{120}$$

The triangular conditions for an even system are expected to be different since all total angular momentum quantum numbers are even. In this case operators belonging to the block $([N/2][N/2],[N/2][N/2])$ are immune to relaxation mechanisms with $k = 1$ and $k = 2$. Operators belonging to any other representation are still affected by relaxation:

$$\Delta(0, k, 0) = 0 \quad \Delta(I, k, I) = 1 \ \forall \ I > 0 \tag{121}$$

For an even number of particles however the representation that is immune to relaxation is D^0 with $d_0 = 1$ and the multiplicity of the $[N/2][N/2]$ irreducible representation is given by $m_{[N/2][N/2]} = 1$. As a consequence an additional splitting of the $([N/2][N/2], [N/2][N/2])$ subspace is impossible and the number of long-lived spin operators is given by corollaries III.1.1 and III.1.2. So in contrast to an odd number of spin-1/2 particles suppression of particular relaxation mechanisms for an even number of spin-1/2 particles does not have an effect on the total number of long-lived operators. The number of long-lived populations and coherences for $N \in \{2, 4, 6\}$ is given in table IX.

N	$N_{\mathrm{LLS}}^{\mathrm{P}}$	$N_{\mathrm{LLS}}^{\mathrm{C}}$	N_{LLS}
2	2	0	2
4	6	8	14
6	20	112	132

Table IX. The number of long-lived spin operators and spin coherences for an even number of spin-1/2 particles experiencing relaxation mechanisms with $k \in \{1, 2\}$.

V.   SYSTEMS OF SPIN-1 PARTICLES

In contrast to spin-1/2 systems a general discussion for spin-1 particles becomes difficult. This is due to the fact that the rotational-permutational dual-pairing is not unique anymore. As a consequence one has to consider all possible triangular conditions occurring in equation 107.

To illustrate the general strategy we consider three identical spin-1 particles These could for example represent a deuterated methyl rotor. According to equation 67 such systems are able to support irreducible representations [3], [21] and [111] of S$_3$ which pair with irreducible representations $D^1 \oplus D^3$, $D^1 \oplus D^2$ and D^0 of SO(3), respectively. Application of corollaries III.1.1 and III.1.2 indicate that the number of long-lived spin operators is bounded by $N_{\mathrm{LLS}} \geq 1 + 1 + 4 \geq 6$. To take rotational symmetries into account the relaxation superoperator is first expressed in the outer tensor basis constructed from the symmetry adapted basis states $\mathcal{B}_{\mathrm{SO}(3)}^{\mathrm{S}_n}$. The matrix representation of $\hat{\mathcal{R}}^{\mathrm{S}_n^2}$ takes the following form

$$\hat{\mathcal{R}}^{\mathrm{S}_n^2} =$$

	[3][3]	[21][21]	[111][111]	[3][21]	[3][111]	[21][111]	[21][3]	[111][3]	[111][21]
[3][3]	■	0	0	0	0	0	0	0	0
[21][21]	0	■	0	0	0	0	0	0	0
[111][111]	0	0	■	0	0	0	0	0	0
[3][21]	0	0	0	■	0	0	0	0	0
[3][111]	0	0	0	0	■	0	0	0	0
[21][111]	0	0	0	0	0	■	0	0	0
[21][3]	0	0	0	0	0	0	■	0	0
[111][3]	0	0	0	0	0	0	0	■	0
[111][21]	0	0	0	0	0	0	0	0	■

$$. \tag{122}$$

Similar to spin-1/2 systems relaxation for spin-1 systems is driven by relaxation mechanisms with $k \in \{1, 2\}$ and only a finite number of triangular conditions has to be considered. The diagonal symmetry blocks $([\lambda][\lambda], [\lambda][\lambda])$ are of special importance since they contain the projection operators $P_{\gamma\delta}^{[\lambda]}$.

The dual pairing for the $([3][3], [3][3])$ symmetry block requires the following triangular conditions

$$\Delta(1, 1, 3) = 0,$$
$$\Delta(I_1, 2, I_2) = 1 \quad \text{for} \quad I_1, I_2 \in \{1, 3\}, \tag{123}$$
$$\Delta(I, 1, I) = 1 \quad \text{for} \quad I \in \{1, 3\}.$$

The required triangular conditions for dual pairing within the $([21][21], [21][21])$ symmetry block does not lead to any rotational constraints

$$\Delta(I_1, k, I_2) = 1 \quad \text{for} \quad I_1, I_2 \in \{1, 2\}. \tag{124}$$

The $([111][111], [111][111])$ symmetry subspace couples uniquely to D^0 and is rotationally invariant so that all triangular conditions vanish identically

$$\Delta(0, k, 0) = 0. \tag{125}$$

This indicates that if both $k = 1$ and $k = 2$ relaxation mechanisms are active, the number of long-lived spin operators is given by corollaries III.1.1 and III.1.2. On the other hand if only

$k = 1$ relaxation mechanisms are active an increased number of long-lived spin operators should be expected.

For example, the rotationally invariant symmetry block $([111][111], [111][111])$ is one-dimensional (there is only one spin-state with $I = 0$) and contributes one long-lived operator even if relaxation mechanisms are constrained to $k = 1$. But for the fully symmetric symmetry block $([3][3], [3][3])$ equation 123 indicates that relaxation terms with $k = 1$ cannot induce transitions between states with $I = 1$ and $I = 3$. The projector $P_{\gamma\delta}^{[3]}$ however contains contributions from spin states with $I = 1$ and $I = 3$. This may be seen by expressing $P_{\gamma\delta}^{[3]}$ in terms of symmetry adapted states

$$P_{\gamma\delta}^{[3]} = \sum_{m=-1}^{+1} |[3], \gamma, 1, m\rangle\langle[3], \delta, 1, m| + \sum_{m=-3}^{3} |[3], \gamma, 3, m\rangle\langle[3], \delta, 3, m| = P_{\gamma\delta}^{[3]1} + P_{\gamma\delta}^{[3]3}, \quad (126)$$

with $P_{\gamma\delta}^{[\lambda]I}$ being the projector onto the $[\lambda]$ subspace with total angular momentum I. The triangular conditions above then imply that both $P_{\gamma\delta}^{[3]1}$ and $P_{\gamma\delta}^{[3]3}$ are decoupled and members of the nullspace $\mathrm{Null}(\hat{\mathcal{R}}^{S_n^2})$

$$\hat{\mathcal{R}}^{S_n^2}|P_{\gamma\delta}^{[3]1}) = |0) \quad \text{and} \quad \hat{\mathcal{R}}^{S_n^2}|P_{\gamma\delta}^{[3]3}) = |0). \quad (127)$$

The projector $P_{\gamma\delta}^{[3]}$ is thus split into two long-lived spin operators. Finally, according to equation 124 the diagonal symmetry block $([21][21], [21][21])$ is not subjected to any rotational selection rules. The number of long-lived spin operators taking rotational symmetries into account increases from $N_{\mathrm{LLS}} \geq 6$ to $N_{\mathrm{LLS}} \geq 1 + 2 + 4 \geq 7$.

A comparison with numerical results however shows that this number is greatly exceeded. For three identical spin-1 particles dominated by relaxation mechanisms with $k = 1$ the nullspace $\mathrm{Null}(\hat{\mathcal{R}}^{S_n^2})$ consists of 15 elements and not 7. Some of this discrepancy may be explained by yet another rotational selection rule specific to linear relaxation terms with $k = 1$. This selection rule is not captured by 107 but may be derived as follows. The outer tensor basis of symmetry adapted basis states are eigenoperators of the left and right multiplication superoperator of I^2

$$
\begin{aligned}
(I^2 \otimes \mathbb{1})|[\lambda], I_1; [\kappa], I_2) &= I_1(I_1 + 1)|[\lambda], I_1; [\kappa], I_2), \\
(\mathbb{1} \otimes I^2)|[\lambda], I_1; [\kappa], I_2) &= I_2(I_2 + 1)|[\lambda], I_1; [\kappa], I_2),
\end{aligned}
\quad (128)
$$

where we have suppressed the group and z-angular momentum projection number. As shown in appendix A 4 the effective double commutation superoperator $\hat{A}_{1m}^{[N]}\hat{A}_{1m}^{[N],\dagger}$ additionally com-

mutes with both the left and right multiplication superoperator of I^2

$$[\hat{A}_{1m}^{[N]}\hat{A}_{1m}^{[N],\dagger}, (I^2 \otimes \mathbb{1})] = 0 \quad \text{and} \quad [\hat{A}_{1m}^{[N]}\hat{A}_{1m}^{[N],\dagger}, (\mathbb{1} \otimes I^2)] = 0. \tag{129}$$

The vanishing commutator leads to two additional symmetry constraints. A relaxation superoperator $\hat{\mathcal{R}}^{S_n^2}$ with $k = 1$ being the only active relaxation mechanism has to preserve both total angular momentum quantum numbers I_1 and I_2 of an operator $|[\lambda], I_1; [\kappa], I_2)$

$$\hat{\mathcal{R}}^{S_n^2}(I^2 \otimes \mathbb{1})|[\lambda], I_1; [\kappa], I_2) = I_1(I_1 + 1)\hat{\mathcal{R}}^{S_n^2}|[\lambda], I_1; [\kappa]) = (I^2 \otimes \mathbb{1})\hat{\mathcal{R}}^{S_n^2}|[\lambda], I_1; [\kappa], I_2),$$
$$\hat{\mathcal{R}}^{S_n^2}(\mathbb{1} \otimes I^2)|[\lambda], I_1; [\kappa], I_2) = I_2(I_2 + 1)\hat{\mathcal{R}}^{S_n^2}|[\lambda], I_1; [\kappa]) = (\mathbb{1} \otimes I^2)\hat{\mathcal{R}}^{S_n^2}|[\lambda], I_1; [\kappa], I_2). \tag{130}$$

This type of symmetry has implications for diagonal symmetry blocks that are not uniquely associated with a single total angular momentum quantum number. For example, the symmetry block $([21][21], [21][21])$ associated with angular momentum states with $I = 1$ and $I = 2$ is not subjected to triangular conditions, but is subjected to this additional type of symmetry. In particular this means, similar to the projector $P_{\gamma\delta}^{[3]}$, the projector $P_{\gamma\delta}^{[21]}$ may be decomposed according to its total angular moment components

$$P_{\gamma\delta}^{[21]} = \sum_{m=-1}^{+1} |[21], \gamma, 1, m\rangle\langle[21], \delta, 1, m| + \sum_{m=-2}^{+2} |[21], \gamma, 2, m\rangle\langle[21], \delta, 2, m| = P_{\gamma\delta}^{[21]1} + P_{\gamma\delta}^{[21]2}. \tag{131}$$

Since the irreducible representation [21] pairs with two distinct total angular momentum numbers the number of long-lived spin operators contributed by the $([21][21], [21][21])$ symmetry block increases from 4 to 8. The total number of long-lived spin operators is then bounded by $N_{\text{LLS}} \geq 1 + 2 + 2 \times 4 \geq 11$. It is clear that this result is readily generalised to larger identical spin systems with $I = 1$.

A small caveat remains however. As mentioned previously numerical results indicate that the exact number of long-lived spin operators is given by $N_{\text{LLS}} = 15$. Numerical analysis shows that these operators are members of the $([3][21], [3][21])$ and $([21][3], [21][3])$ subspace. At this point we are not able to systematically identify these operators as they do not result from further splittings of the projection operators.

VI.   DUAL-SYMMETRY BASIS SETS

For practical applications we will briefly outline a method to construct dual-symmetry adapted basis states. A thorough discussion of the necessary group theoretical tools, including proofs, may be found in reference 47.

For a given group G_0 define a *class operator C_{G_0}* as follows

$$C_{G_0} = \sum_{g \in \mathrm{Cl}(h)} g, \tag{132}$$

with h being an arbitrary class representative. The class operator C_{G_0} commutes with every element in G_0

$$[C_{G_0}, g] = 0 \quad \forall g \in G_0 \tag{133}$$

and each class operator C_{G_0} possesses a complete set of eigenstates $\{|\phi_j\rangle\}$

$$C_{G_0}|\phi_j\rangle = \zeta_{G_0}^j |\phi_j\rangle \quad \text{and} \quad \langle\phi_j|\phi_k\rangle = \delta_{jk}. \tag{134}$$

In agreement with quantum mechanical convention the eigenstates may be labelled according to their eigenvalues $\zeta_{G_0}^j$

$$\{|\zeta_{G_0}^1\rangle, |\zeta_{G_0}^2\rangle, \ldots, |\zeta_{G_0}^{N_{\mathbb{H}}}\rangle\}. \tag{135}$$

The eigenvalues $\{\zeta_{G_0}^j\}$ are related to the irreducible characters of G_0. If the group G_0 is abelian the set of eigenvalues $\{|\zeta_{G_0}^1\rangle, |\zeta_{G_0}^2\rangle, \ldots, |\zeta_{G_0}^{N_{\mathbb{H}}}\rangle\}$ will be non-degenerate and every eigenstate may be uniquely specified by a single eigenvalue. In this case the set of eigenstates $\{|\zeta_{G_0}^1\rangle, |\zeta_{G_0}^2\rangle, \ldots, |\zeta_{G_0}^{N_{\mathbb{H}}}\rangle\}$ spans all irreducible representations Γ_j of G_0.

In general the set of eigenvalues $\{\zeta_{G_0}^j\}$ will be degenerate since a single eigenvalue or character is not enough to distinguish between basis states belonging to the same irreducible representation Γ_j with $d_{\Gamma_j} > 1$. To uniquely address an eigenstate $|\phi\rangle$ it is necessary to assign additional quantum numbers to each state. The additional quantum numbers are provided by class operators of a given subgroup of G_0. For example if $G_1 \subset G_0$ and C_{G_1} is a class operator of G_1 equation 133 indicates that C_{G_1} and C_{G_0} commute

$$[C_{G_0}, C_{G_1}] = 0, \tag{136}$$

so that C_{G_1} and C_{G_0} share a common set of eigenstates $|\zeta_{G_0}^j, \zeta_{G_1}^j\rangle$.

The idea is to add class operators of the subgroup chain $G_N \subset \cdots \subset G_1 \subset G_0$ until the set of eigenvalues $\{\zeta_{G_0}^j, \zeta_{G_1}^j, \ldots, \zeta_{G_N}^j\}$ uniquely labels each eigenstate $|\phi_j\rangle$. The subgroup chain is called *canonical* if the group G_N is abelian. In this case there is no need to add any further operators and the degeneracy is completely lifted. The set of class operators $\mathcal{C}_G = \{C_{G_0}, C_{G_1}, \ldots\}$ is then called a *complete set of commuting operators* (CSCO).

For the rotation group SO(3) the class operator is given by I^2. To resolve possible degeneracies the class operator I_z for the subgroup chain SO(2) $\subset$ SO(3) is added to the CSCO

$$\mathcal{C}_{\text{SO(3)}} = \{I^2, I_z\}. \tag{137}$$

To construct rotational-permutational symmetry adapted basis sets class operators of the group S_n are added to the SO(3) CSCO. This is possible since every permutation operator P_σ commutes with I^2 and I_z.

As an example we consider a system of three identical spins. A possible choice for the CSCO is given by the following set of operators

$$\mathcal{C}_{\text{SO(3)}}^{S_n} = \{I^2, I_z, P_{12} + P_{13} + P_{23}, P_{123}\}, \tag{138}$$

which characterises the subgroup chains SO(2) $\subset$ SO(3) and $A_3 \subset S_3$. The dual-symmetry adapted basis is calculated by numerically solving for the eigenstates of the matrix pencil of $\mathcal{C}_{\text{SO(3)}}^{S_n}$

$$(a_1 I^2 + a_2 I_z + a_3(P_{12} + P_{13} + P_{23}) + a_4 P_{123})|\phi_j\rangle = (a_1 I(I+1) + a_2 m + a_3 \zeta_{S_3}^j + a_4 \zeta_{A_3}^j)|\phi_j\rangle. \tag{139}$$

For a system of three spin-1/2 particles the solution to the matrix pencil of equation 139 leads to the following set of states

$$\mathcal{B}_{\text{SO(3)}}^{S_n} =$$

$$
\begin{cases}
|[1], 1, 3/2, -3/2\rangle = |\beta\beta\beta\rangle \\[4pt]
|[1], 1, 3/2, -1/2\rangle = \frac{1}{\sqrt{3}}(|\beta\beta\alpha\rangle + |\beta\alpha\beta\rangle + |\alpha\beta\beta\rangle) \\[4pt]
|[1], 1, 3/2, +1/2\rangle = \frac{1}{\sqrt{3}}(|\alpha\alpha\beta\rangle + |\alpha\beta\alpha\rangle + |\beta\alpha\alpha\rangle) \\[4pt]
|[1], 1, 3/2, +3/2\rangle = |\alpha\alpha\alpha\rangle \\[4pt]
|[21], 1, 1/2, -1/2\rangle = \frac{1}{\sqrt{3}}(|\beta\beta\alpha\rangle + \epsilon|\beta\alpha\beta\rangle + \epsilon^*|\alpha\beta\beta\rangle) \\[4pt]
|[21], 2, 1/2, -1/2\rangle = \frac{1}{\sqrt{3}}(|\beta\beta\alpha\rangle + \epsilon^*|\beta\alpha\beta\rangle + \epsilon|\alpha\beta\beta\rangle) \\[4pt]
|[21], 1, 1/2, +1/2\rangle = \frac{1}{\sqrt{3}}(|\alpha\alpha\beta\rangle + \epsilon|\alpha\beta\alpha\rangle + \epsilon^*|\beta\alpha\alpha\rangle) \\[4pt]
|[21], 2, 1/2, +1/2\rangle = \frac{1}{\sqrt{3}}(|\alpha\alpha\beta\rangle + \epsilon^*|\alpha\beta\alpha\rangle + \epsilon|\beta\alpha\alpha\rangle)
\end{cases}
\tag{140}
$$

$$\text{with} \quad \epsilon = \exp(-i\frac{2\pi}{3}).$$

38

Each state possesses definite permutation symmetry $[\lambda]$ with group projection number γ and definite total angular momentum I with z- angular momentum m. A state $|[\lambda], \gamma, I, m\rangle$ is therefore uniquely characterised by the set of quantum numbers $\{[\lambda], \gamma, I, m\}$.

VII. AN ILLUSTRATIVE NMR EXAMPLE

Making use of the concepts presented in section IV and VI we examine the possible long-lived spin operators for protonated methyl rotors. Such systems have been analysed previously using purely rotational and permutational selection rules, but not under dual-selection rules[5,15]. In the rotating frame the coherent Hamiltonian of the system is given by a symmetric scalar coupling term

$$\mathcal{H}_{\mathrm{coh}} = 2\pi J(\mathbf{I}_1 \cdot \mathbf{I}_2 + \mathbf{I}_1 \cdot \mathbf{I}_3 + \mathbf{I}_2 \cdot \mathbf{I}_3). \tag{141}$$

The system therefore displays S_3 symmetry and classifies as an odd spin-1/2 system. For such a case the arguments of section IV A indicate that dual-selection rules may lead to an increased number of long-lived spin operators.

The required degree of symmetry is a consequence of overall tumbling and internal methyl rotor dynamics. As illustrated in figure 1 the methyl rotor is assumed to be attached to a marcomolecule undergoing isotropic rotational diffusion characterised by a single correlation time τ_c. The methyl rotor dynamics are described by a symmetric three-fold nearest neighbour jump model with rate constant $k = (3\tau_r)^{-1}$.
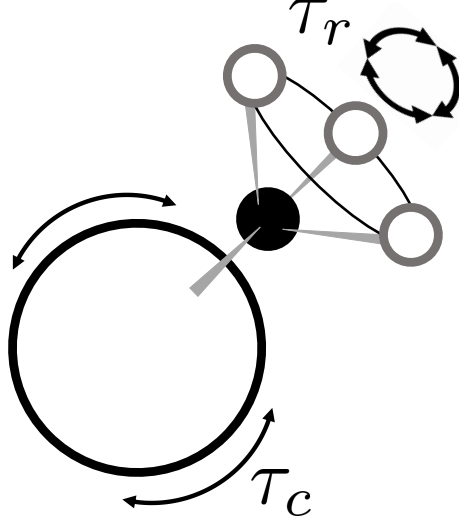
Figure 1. Motional model for a methyl rotor attached to a tumbling macromolecule. The methyl rotor performs symmetric three-fold jumps around its symmetry axis with a jump rate $k = (3\tau_r)^{-1}$. At the same time the methyl rotor, being attached to the macromolecule, experiences isotropic rotational diffusion characterised by a correlation time τ_c. For this setup, rotational diffusion is much slower than the methyl group reorientation ($\tau_r \ll \tau_c$) resulting in a reasonable timescale separation of the two stochastic processes.

Focusing on dominant dipolar relaxation mechanisms, the relaxation superoperator takes the form[61,62]

$$\hat{\mathcal{R}} = - b_{\text{HH}}^2 \sum_{\substack{i<j=1 \\ k<l=1}}^{3} \int_{-\infty}^{0} C_{ijkl}(\tau)d\tau \sum_{m=-2}^{+2} \hat{T}_{2m}^{ij} \hat{T}_{2m}^{kl,\dagger}, \quad \text{with} \quad b_{\text{HH}} = -\frac{\mu_0}{4\pi} \frac{\gamma_{\text{H}}^2 \hbar}{r_{\text{HH}}^3}, \qquad (142)$$

where b_{HH} represents the proton-proton dipolar coupling strength, r_{HH} the proton-proton distance, γ_{H} the proton gyromagnetic ratio and μ_0 the magnetic constant. The commutation superoperators $\hat{T}_{2m}^{ij}$ are constructed from irreducible spherical tensor given in appendix A 5 and $C^{ijkl}(\tau)$ are (classical) time correlation functions. As shown in appendix A 6 the time correlation functions (including tumbling and methyl rotation) may be expressed as a sum of S_3^2-symmetric and S_3^2-asymmetric contributions

$$C_{ijkl}(\tau) = C_{ijkl}^{\text{sym}}(\tau) + C_{ijkl}^{\text{asym}}(\tau), \qquad (143)$$

40

where

$$
\begin{aligned}
C_{ijkl}^{\text{sym}}(\tau) =& \frac{3}{10} \exp\left(-|\tau|/\tau_c\right), \\
C_{ijkl}^{\text{asym}}(\tau) =& \frac{9}{20} \exp\left(-|\tau|/\tau_c\right) \exp\left(-|\tau|/\tau_r\right)(3\delta_{ik}\delta_{jl} - 1)
\end{aligned}
\tag{144}
$$

and $C_{ijkl}^{\text{sym}}(\tau)$ does not depend upon the indices (i, j, k, l). The relaxation superoperator may then be split into an S_3^2-symmetric and S_3^2-asymmetric term

$$
\begin{aligned}
\hat{\mathcal{R}} =& \hat{\mathcal{R}}_{\text{sym}}^{S_n^2} + \hat{\mathcal{R}}_{\text{asym}}^{S_n^2}, \\
\hat{\mathcal{R}}_{\text{sym}}^{S_n^2} =& -b_{\text{HH}}^2 \sum_{\substack{i<j=1 \\ k<l=1}}^{3} \int_{-\infty}^{0} C_{ijkl}^{\text{sym}}(\tau)d\tau \sum_{m=-2}^{+2} \hat{T}_{2m}^{ij}\hat{T}_{2m}^{kl,\dagger}, \\
\hat{\mathcal{R}}_{\text{asym}}^{S_n^2} =& -b_{\text{HH}}^2 \sum_{\substack{i<j=1 \\ k<l=1}}^{3} \int_{-\infty}^{0} C_{ijkl}^{\text{asym}}(\tau)d\tau \sum_{m=-2}^{+2} \hat{T}_{2m}^{ij}\hat{T}_{2m}^{kl,\dagger}.
\end{aligned}
\tag{145}
$$

For sufficiently short methyl rotor correlation times ($\tau_r \ll \tau_c$), the asymmetric term may be neglected and the methyl rotor dynamics lead to a motional averaging effect. The dipolar relaxation superoperator is then approximated by

$$
\hat{\mathcal{R}} \approx \hat{\mathcal{R}}_{\text{sym}}^{S_n^2}.
\tag{146}
$$

This situation correspond to the first row of table VIII and a total number of $N_{\text{LLS}} = 17$ is expected.

The relaxation superoperator given by equation 146 has been evaluated numerically making use of the symmetry adapted basis given by equation 140. The resulting matrix representation is given in figure 2.

The matrix representation can be seen to match the pattern indicated by equation 114. As a consequence one long-lived spin operators originates from the total population of the [3] symmetry manifold with the remaining 16 long-lived spin operators being elements of the [21] symmetry manifold.

VIII.   CONCLUSIONS

To summarise, we have described a purely group theoretical framework to analyse long-lived spin operators under rotational and permutational symmetries and rotational-permutational dual-symmetries. We have considered systems for which the symmetry of
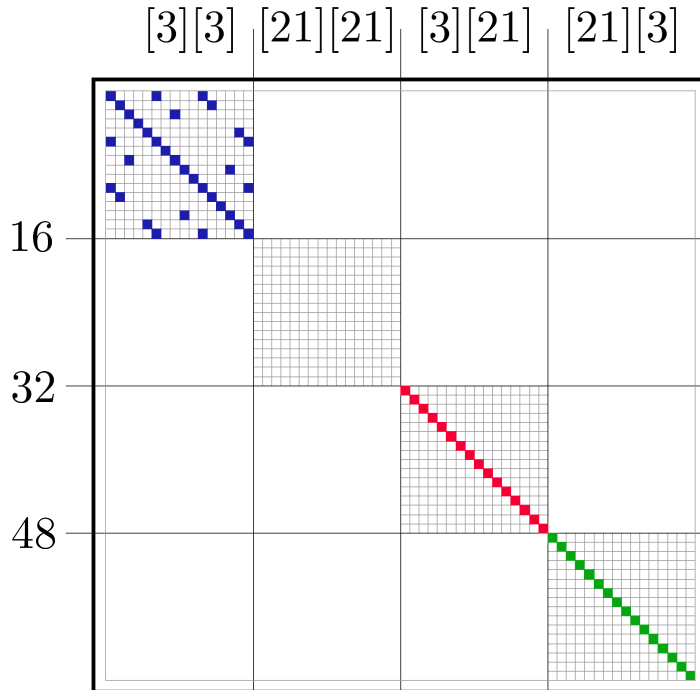
Figure 2. Superoperator matrix representation of the relaxation superoperator given by 146. The matrix representation has been constructed using an outer tensor basis resulting from the symmetry adapted basis states defined by equation 140. Matrix blocks are labelled according to the irreducible representations $[\lambda]$ of S_3. The dimensionality of each block is indicated on the left. Calculations have been performed using *SpinDynamica*[81].

the system may be described by the symmetric group S_n. In this case we have shown, against common belief, that the relaxation superoperator has to be invariant under the direct product group $S_n \otimes S_n^*$ and not S_n for exact long-lived spin order to exist. For systems that do not display any further symmetries we have given an exact number of long-lived states and coherences. For systems with additional rotational symmetries we have derived several lower bounds on the number of long-lived spin operators. This has been achieved by first characterising the symmetries of the system according to the symmetric group S_n and then including rotational selection rules by virtue of the Schur-Weyl duality theorem. For spin-1/2 systems we have given a complete characterisation of long-lived spin operators under such rotational and permutational dual-symmetries.

An increase in the number of long-lived spin operators for spin-1/2 systems is only expected if relaxation is dominated by spherical interactions of rank two and an odd number

of particles. For such systems we have given analytic expressions for the total number of long-lived spin populations and coherences. The treatment of rotational-permutational dual-symmetries of spin systems with $I > 1/2$ have been outlined by considering a system of three identical spin-1 particles.

The discussion for particles with higher spin quantum numbers is complicated due to the loss of uniqueness of rotational and permutation dual pairings. In general for systems with $I > 1$ that are subjected to relaxation mechanisms with spherical rank one or two dual-symmetries do not lead to an increase in the number of long-lived spin operators. For systems dominated by linear relaxation mechanisms with spherical rank one we have identified additional rotational selection rules that are not captured by the Wigner-Eckart theorem. These may be used to partially explain the increase in the number of long-lived spin operators and tighten the lower bound.

Although the discussion has been mostly based on the symmetric group S_n the arguments may readily be extended to other finite groups G. In certain situations the symmetric group S_n may not be the appropriate group to describe the symmetries of the systems. Instead the Hamiltonian and relaxation superoperator are invariant under a smaller permutation group G. But since any finite group G is isomorphic to some subgroup of S_n the rotational and permutational dual-pairing for the subgroup G may be derived by considering branching rules of irreducible representations of S_n to the irreducible representations of G.

Many of the commonly encountered long-lived spin order components fall into this category. We have illustrated this by considering a protonated methyl rotor, but a separate publication is under preparation that applies the presented concepts to a broader series of practical NMR examples.

ACKNOWLEDGMENTS

Appendix A: Appendices

1.   Dimensionality of S_n irreducible representations

The irreducible representations of S_n are in a one-to-one relation with the integers partitions of n. A graphical representation of an integer partition is given by a so-called *Young-Tableau*[44]. For an integer partition $[\lambda_1\lambda_2\lambda_3\ldots]$ the corresponding Young-Tableau displays λ_1 cells in its first row, λ_2 cells in its second row, λ_3 cells in its third row, etc. The integer partitions $\lambda \vdash 3$ with their corresponding Young-Tableau are indicated below

$$[3] \leftrightarrow \square\square\square, \quad [21] \leftrightarrow \square\square\,\square, \quad [111] \leftrightarrow \square\,\square\,\square. \tag{A1}$$

Given a Young-Tableau $[\lambda]$ the *hook* $h_{ij}^{[\lambda]}$ of its cell in the i'th row and j'th column counts the number of cells below and to the right of it (including the cell itself). For the Young-Tableaux of equation A1 the hooks for the individual cells are given by the following:

$$\boxed{3\,2\,1}, \quad \begin{array}{cc}\boxed{3}\,\boxed{1}\\ \boxed{1}\end{array}, \quad \begin{array}{c}\boxed{3}\\ \boxed{2}\\ \boxed{1}\end{array}. \tag{A2}$$

The dimensionality $d_{[\lambda]}$ of a given irreducible representation $[\lambda]$ of S_n is given the *hook length formula*[44]

$$d_{[\lambda]} = \frac{n!}{\prod_{ij} h_{ij}^{[\lambda]}} \tag{A3}$$

For small groups such as S_3 this may be verified by explicit calculation

$$d_{[3]} = \frac{3!}{3 \times 2 \times 1} = 1, \; d_{[21]} = \frac{3!}{3 \times 1 \times 1} = 2, \; d_{[111]} = \frac{3!}{3 \times 2 \times 1} = 1. \tag{A4}$$

To determine the hook length product for a generic Young-Tableau $[\lambda_1\lambda_2]$ it is advantageous to split the Young-Tableau as shown below

$$\tag{A5}$$

It is easy to see that the blue squares contribute a factor of $\lambda_2!$ and the red squares a factor of $(\lambda_1 - \lambda_2)!$. The hook length product for the black squares is given by the following pattern

$$(\lambda_1 + 1)(\lambda_1 + 1 - 1)\ldots(\lambda_1 + 1 - (\lambda_2 - 1)) = \frac{(\lambda_1 + 1)!}{(\lambda_1 - \lambda_2 + 1)!}. \tag{A6}$$

Collecting all factors leads to the following product of hook lengths

$$\frac{\lambda_2!(\lambda_1 - \lambda_2)!(\lambda_1 + 1)!}{(\lambda_1 - \lambda_2 + 1)!} = \frac{\lambda_2!(\lambda_1 + 1)!}{(\lambda_1 - \lambda_2 + 1)}. \tag{A7}$$

The dimensionality of an irreducible representation $d_{[\lambda]}$ with maximal length two is then given by the expression below

$$(\lambda_1 + \lambda_2)! \left(\frac{\lambda_2!(\lambda_1 + 1)!}{(\lambda_1 - \lambda_2 + 1)} \right)^{-1} = (\lambda_1 + \lambda_2)! \frac{(\lambda_1 - \lambda_2 + 1)}{\lambda_2!(\lambda_1 + 1)!}. \tag{A8}$$

This is the expression given in equation 69. Similar arguments may then be used to derive an expression for the dimensionality of irreducible representation associated with integer partitions of maximal length three.

2. Inner products

Given two irreducible representations $D^{\Gamma_j^a}(g^a)$ and $D^{\Gamma_j^b}(g^a)$ of the groups G_a and G_b the character of the resulting direct product representation is given by the following expression

$$\mathrm{Tr}(D^{\Gamma_j^a, \Gamma_k^b}(g^a, g^b)) = \mathrm{Tr}(D^{\Gamma_j^a}(g^a) \otimes D^{\Gamma_k^b}(g^b)) = \chi^{\Gamma_j^a}(g^a)\chi^{\Gamma_k^b}(g^b). \tag{A9}$$

For the case that the two groups are identical

$$G_a = G, \quad G_b = G \tag{A10}$$

and the group products are restricted to the diagonal case:

$$D(g, g) = D(g) \otimes D(g), \tag{A11}$$

one speaks of an *inner product* of group representations. In this case the product character of equation A9 reduces the the expression below

$$\mathrm{Tr}(D^{\Gamma_j \times \Gamma_k}(g, g)) = \mathrm{Tr}(D^{\Gamma_j}(g) \otimes D^{\Gamma_k}(g)) = \chi^{\Gamma_j}(g)\chi^{\Gamma_k}(g). \tag{A12}$$

The product character $\chi^{\Gamma_j}(g)\chi^{\Gamma_k}(g)$ is in general not an irreducible character of G so that the representation $D^{\Gamma_j \times \Gamma_k}(g, g)$ is reducible. The reduction of the inner product follows a *Clebsch-Gordan series*

$$\Gamma^j \times \Gamma^k = \bigoplus_{p=1}^{N_\Gamma} m_p^{jk} \, \Gamma^p, \tag{A13}$$

where m_p^{jk} represents the multiplicity of the irreducible representation Γ^p for the reduction $\Gamma^j \times \Gamma^k$. The multiplicities m_p^{jk} may be determined from the characters of the irreducible representations

$$m_p^{jk} = \frac{1}{|G|} \sum_{g \in G} \chi^{\Gamma_j}(g) \chi^{\Gamma_k}(g) \chi^{\Gamma_{p,*}}(g), \tag{A14}$$

which follows from the Schur-orthogonality relations given by equation 23.

Similar concepts hold for some continuous groups. In particular for the rotation group SO(3) the inner product reduction is given by the well-known angular momentum coupling rule

$$D^{I_1 \times I_2} = \bigoplus_{I=|I_1-I_2|}^{I_1+I_2} D^I. \tag{A15}$$

Such general rules for Clebsch-Gordan series are an exception however.

3. Dual-pairing in Liouville space

The dual-pairings indicated by equation 58 apply to basis elements of $\mathbb{H}$. In certain cases it might be useful to extend rotational-permutational dual-pairings to $\mathbb{L}(\mathbb{H})$. Here rotational and permutation dual-pairings refer to the pairing of irreducible representations for rotations in $\mathbb{L}(\mathbb{H})$ and permutations generated by the set

$$\{\hat{P}_\sigma^\sigma\} = \{\hat{P}_\sigma\} \quad \sigma \in S_n, \tag{A16}$$

which generates a representation of S_n on $\mathbb{L}(\mathbb{H})$.

According to equation 31 $\mathbb{L}(\mathbb{H})$ is given by a tensor product of $\mathbb{H}$ and its dual space $\mathbb{H}^*$. Applying the Schur-Weyl duality twice we may express $\mathbb{L}(\mathbb{H})$ as follows

$$
\begin{aligned}
\mathbb{L}(\mathbb{H}) &= \left(\bigoplus_{\lambda \vdash N}^{l(\lambda) \le n} D^{\{\lambda\}} \circ D^{[\lambda]} \right) \otimes \left(\bigoplus_{\kappa \vdash N}^{l(\kappa) \le n} D^{\{\kappa\}} \circ D^{[\kappa]} \right)^* \\
&= \bigoplus_{\lambda \vdash N}^{l(\lambda) \le n} \bigoplus_{\kappa \vdash N}^{l(\kappa) \le n} D^{\{\lambda\}} \otimes D^{\widetilde{\{\kappa\}}} \circ D^{[\lambda]} \otimes D^{\widetilde{[\kappa]}},
\end{aligned}
\tag{A17}
$$

where $\widetilde{[\lambda]}$ and $\widetilde{\{\lambda\}}$ denote conjugate partitions. The direct product representations translate into group inner products and may be reduced as indicated in section A 2

$$\mathbb{L}(\mathbb{H}) = \bigoplus_{\lambda \vdash N}^{l(\lambda) \le n} \bigoplus_{\kappa \vdash N}^{l(\kappa) \le n} D^{\{\lambda\} \times \widetilde{\{\kappa\}}} \circ D^{[\lambda] \times \widetilde{[\kappa]}}. \tag{A18}$$

As a consequence the operators on $\mathbb{L}(\mathbb{H})$ may always be chosen to transform irreducibly under SO(3) and the set of spin permutation superoperators $\{\hat{P}_\sigma\}$.

We illustrate this by considering a simple example. Consider the dual-pairings given in table V. The operator space $\mathbb{L}(\mathbb{H})$ may then be expressed as shown below

$$\mathbb{L}(\mathbb{H}) = \{D^{\frac{3}{2}} \circ D^{[3]} \oplus D^{\frac{1}{2}} \circ D^{[21]}\} \otimes \{D^{\frac{3}{2}} \circ D^{\widetilde{[3]}} \oplus D^{\frac{1}{2}} \circ D^{\widetilde{[21]}}\}, \tag{A19}$$

where we have replaced $D^{\widetilde{I}}$ by D^I since total angular momentum representations are self-conjugate. Distributing the tensor product and performing the inner product reduction leads to the following

$$\begin{aligned}
\mathbb{L}(\mathbb{H}) = &\{(D^0 \oplus D^1 \oplus D^2 \oplus D^3) \circ D^{[3]}\} \\
&\oplus \{(D^1 \oplus D^2) \circ D^{[21]}\} \\
&\oplus \{(D^1 \oplus D^2) \circ D^{[21]}\} \\
&\oplus \{(D^0 \oplus D^1) \circ (D^{[3]} \oplus^{[21]} \oplus D^{[111]})\}.
\end{aligned} \tag{A20}$$

The relations above do not give a unique dual pairing between S_n and SO(3) on $\mathbb{L}(\mathbb{H})$. To resolve this issue simply follow rule (1) of section III D and distribute the dual-pairings over all direct sums

$$\begin{aligned}
\mathbb{L}(\mathbb{H}) = &\{D^0 \circ D^{[3]} \oplus D^1 \circ D^{[3]} \oplus D^2 \circ D^{[3]} \oplus D^3 \circ D^{[3]}\} \\
&\oplus \{D^1 \circ D^{[21]} \oplus D^2 \circ D^{[21]}\} \\
&\oplus \{D^1 \circ D^{[21]} \oplus D^2 \circ D^{[21]}\} \\
&\oplus \{D^0 \circ D^{[3]} \oplus D^0 \circ D^{[21]} \oplus D^0 \circ D^{[111]} \\
&\quad \oplus\ D^1 \circ D^{[3]} \oplus D^1 \circ D^{[21]} \oplus D^1 \circ D^{[111]}\}.
\end{aligned} \tag{A21}$$

Then according to rule (2) the multiplicity-dimensionality relation is satisfied for each individual pairing

$$\begin{aligned}
\mathbb{L}(\mathbb{H}) = \\
&\{(D^0 \circ D^{[3]}) \oplus (D^1 \circ 3 \times D^{[3]}) \\
&\oplus\ (D^2 \circ 5 \times D^{[3]}) \oplus (D^3 \circ 7 \times D^{[3]})\} \\
&\oplus \{(2 \times D^1 \circ 3 \times D^{[21]}) \oplus (2 \times D^2 \circ 5 \times D^{[21]})\} \\
&\oplus \{(2 \times D^1 \circ 3 \times D^{[21]}) \oplus (2 \times D^2 \circ 5 \times D^{[21]})\} \\
&\oplus \{(D^0 \circ D^{[3]}) \oplus (2 \times D^0 \circ D^{[21]}) \oplus (D^0 \circ D^{[111]}) \\
&\oplus\ (D^1 \circ 3 \times D^{[3]}) \oplus (2 \times D^1 \circ 3 \times D^{[21]}) \oplus (D^1 \circ 3 \times D^{[111]})\}.
\end{aligned} \tag{A22}$$

A quick summation over the symmetry adapted basis elements for S_n or $SO(3)$ shows that the dimensionality of the space is correct:

$$
\begin{aligned}
d_{\mathbb{H}}^2 &= (2 + 2 + 1) + (6 + 18 + 3) + (5 + 20) + (7) \\
&= (2 + 6 + 5 + 7) + (2 + 18 + 20) + (1 + 3) = 64.
\end{aligned}
\tag{A23}
$$

The extension of the duality principle to $\mathbb{L}(\mathbb{H})$ thus enables dual-symmetry characterisation of a set of basis operators without explicit construction. And while calculations of this type become increasingly tedious with an increasing number of spins, the systematic rules outlined are easily implemented into symbolic software packages such as *Mathematica*[82].

4. Commutator of commutation superoperators

A generic commutation superoperator $\hat{Q}$ is defined as follows

$$
\hat{Q} = Q \otimes \mathbb{1} - \mathbb{1} \otimes Q^\dagger = \hat{Q}^{\mathrm{L}} - \hat{Q}^{\mathrm{R}},
\tag{A24}
$$

where $\hat{Q}^{\mathrm{L}}$ and $\hat{Q}^{\mathrm{R}}$ are left and right multiplication superoperators, respectively. These act on an operator X as follows

$$
\hat{Q}^{\mathrm{L}} X = QX \quad \hat{Q}^{\mathrm{R}} X = XQ.
\tag{A25}
$$

Left and right multiplication superoperators for any two operators A and B commute

$$
[\hat{A}^{\mathrm{L}}, \hat{B}^{\mathrm{R}}] = 0.
\tag{A26}
$$

The commutator of two commutation superoperators $\hat{A}$ and $\hat{B}$ may then be derived from their commutator on $\mathbb{H}$

$$
[\hat{A}, \hat{B}] = [\hat{A}^{\mathrm{L}}, \hat{B}^{\mathrm{L}}] - [\hat{A}^{\mathrm{R}}, \hat{B}^{\mathrm{R}}] = [A, B] \otimes \mathbb{1} - \mathbb{1} \otimes [A, B]^\dagger,
\tag{A27}
$$

which follows from the definition of the left and right multiplication superoperators.

The commutator between the effective commutation superoperator $\hat{A}_{1m}^{[N]}$ and the left multiplication superoperator $I^2 \otimes \mathbb{1}$ may then be expressed as follows

$$
[\hat{A}_{1m}^{[N]}, I^2 \otimes \mathbb{1}] = [A_{1m}^{[N]}, I^2] \otimes \mathbb{1} - \mathbb{1} \otimes [A_{1m}^{[N]}, \mathbb{0}]^\dagger = [A_{1m}^{[N]}, I^2] \otimes \mathbb{1}.
\tag{A28}
$$

The spherical tensor operators $A_{1m}^{[N]}$ are linear combinations of the total x-, y-, and z-angular momentum operators

$$
A_{1m}^{[N]} = c_m^x I_x + c_m^y I_y + c_m^z I_z,
\tag{A29}
$$

for some coefficients c_m^μ. But any total angular momentum operator I_μ along a particular Cartesian coordinate axis commutes with the total angular momentum operator I^2. The effective commutation superoperator $\hat{A}_{1m}^{[N]}$ then commutes with the left multiplication superoperator $I^2 \otimes \mathbb{1}$

$$[\hat{A}_{1m}^{[N]}, I^2 \otimes \mathbb{1}] = 0. \tag{A30}$$

In full analogy $\hat{A}_{1m}^{[N]}$ also commutes with the right multiplication superoperator $\mathbb{1} \otimes I^{2,\dagger}$.

As a result any product of the effective commutation superoperator $\hat{A}_{1m}^{[N]}$, and in particular the double commutation superoperator $\hat{A}_{1m}^{[N]} \hat{A}_{1m}^{[N],\dagger}$, commutes with $I^2 \otimes \mathbb{1}$ and $\mathbb{1} \otimes I^{2,\dagger}$.

5. Spherical Tensor Operators

Spherical tensor operators for dipolar interactions are summarised in Table X. A generic operator is denoted by T_{km}^{ij}. The superscript (ij) indicates angular momentum coupling of spins i and j resulting in a spherical tensor operator of total angular momentum k and z-angular momentum m.

$m \backslash k$	2
± 2	$\frac{1}{2} I_1^\pm I_2^\pm$
± 1	$\mp \frac{1}{2} \left(I_1^\pm I_{2z} + I_{1z} I_2^\pm \right)$
0	$-\frac{1}{2\sqrt{6}} \left(I_1^+ I_2^- + I_1^- I_2^+ - 4 I_{1z} I_{2z} \right)$

Table X. Dipolar spherical tensor operators for a coupled spin-1/2 pair.

6. Methyl rotor correlation functions

When expressed in the symmetry frame of the methyl rotor the dipolar interaction tensors W_{ij} take the form

$$W_{12} = \begin{bmatrix} -\frac{5}{4} & \frac{3\sqrt{3}}{4} & 0 \\ \frac{3\sqrt{3}}{4} & \frac{1}{4} & 0 \\ 0 & 0 & 1 \end{bmatrix}, \; W_{13} = \begin{bmatrix} -\frac{5}{4} & -\frac{3\sqrt{3}}{4} & 0 \\ -\frac{3\sqrt{3}}{4} & \frac{1}{4} & 0 \\ 0 & 0 & 1 \end{bmatrix}, \; W_{23} = \begin{bmatrix} 1 & 0 & \\ 0 & -2 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{A31}$$

It is easy to see that the dipolar interaction tensors are related by a three-fold spatial rotation $K_z(2\pi/3)$ around the symmetry axis of the methyl rotor.

Based on the correlation function given in reference 15 we express the dipolar correlation function as follows

$$
\begin{aligned}
C_{ijkl}(\tau) &= \frac{1}{5}\exp\left(-|\tau|/\tau_c\right)C_{ijkl}^{\mathrm{rot}}(\tau) \\
C_{ijkl}^{\mathrm{rot}}(\tau) &= \langle \mathrm{Tr}\{K_z(\Omega_0)W_{ij}K_z^{\mathrm{T}}(\Omega_0 - \Omega_\tau)W_{kl}^{\mathrm{T}}K_z^{\mathrm{T}}(\Omega_\tau)\}\rangle_{\mathrm{rot}}
\end{aligned}
\tag{A32}
$$

Here Ω_t is a random variable taking on values from the set $\{0, 2\pi/3, 4\pi/4\}$ at time t and $\langle\dots\rangle_{\mathrm{rot}}$ represents an ensemble average over the methyl rotor dynamics. The purely rotational correlation function $C_{ijkl}^{\mathrm{rot}}(\tau)$ may be split into its mean and difference

$$
C_{ijkl}^{\mathrm{rot}}(\tau) = \mathrm{Tr}\{W_{ij}^{\Sigma}W_{kl}^{\Sigma,\mathrm{T}}\} + \langle \mathrm{Tr}\{K_z(\Omega_0)W_{ij}^{\Delta}K_z^{\mathrm{T}}(\Omega_0 - \Omega_\tau)W_{kl}^{\Delta,\mathrm{T}}K_z^{\mathrm{T}}(\Omega_\tau)\}\rangle_{\mathrm{rot}},
\tag{A33}
$$

with W_{ij}^{Σ} being the methyl rotor averaged dipolar tensor and $W_{ij}^{\Delta} = W_{ij} - W_{ij}^{\Sigma}$. With this definition it is easy to see that

$$
C_{ijkl}(\tau) = C_{ijkl}^{\mathrm{sym}}(\tau) + C_{ijkl}^{\mathrm{asym}}(\tau),
\tag{A34}
$$

where we have defined

$$
\begin{aligned}
C_{ijkl}^{\mathrm{sym}}(\tau) &= \frac{1}{5}\exp\left(-|\tau|/\tau_c\right)\mathrm{Tr}\{W_{ij}^{\Sigma}W_{kl}^{\Sigma,\mathrm{T}}\}, \\
C_{ijkl}^{\mathrm{asym}}(\tau) &= \frac{1}{5}\exp\left(-|\tau|/\tau_c\right) \times \langle \mathrm{Tr}\{K_z(\Omega_0)W_{ij}^{\Delta}K_z^{\mathrm{T}}(\Omega_0 - \Omega_\tau)W_{kl}^{\Delta,\mathrm{T}}K_z^{\mathrm{T}}(\Omega_\tau)\}\rangle_{\mathrm{rot}}.
\end{aligned}
\tag{A35}
$$

The rotational mean and correlation function may evaluated by considering the angular transition density $T_\tau(\Omega_n|\Omega_m)$

$$
\langle \mathrm{Tr}\{K_z(\Omega_0)W_{ij}^{\Delta}K_z^{\mathrm{T}}(\Omega_0 - \Omega_\tau)W_{kl}^{\Delta,\mathrm{T}}K_z^{\mathrm{T}}(\Omega_\tau)\}\rangle_{\mathrm{rot}} =
\tag{A36}
$$

$$
\frac{1}{3}\sum_{m,n=1}^{3}\mathrm{Tr}\{K_z(\Omega_m)W_{ij}^{\Delta}K_z^{\mathrm{T}}(\Omega_m - \Omega_n)W_{kl}^{\Delta,T}K_z^{\mathrm{T}}(\Omega_n)T_\tau(\Omega_n|\Omega_m)\}.
$$

$$
W_{ij}^{\Sigma} = \frac{1}{3}\sum_{i,j=1}^{3}K_z(\Omega_n)W_{ij}^{\Delta}K_z^{\mathrm{T}}(\Omega_n)T_\tau(\Omega_n|\Omega_m)
\tag{A37}
$$

For the symmetric three-fold jump model $T_\tau(\Omega_n|\Omega_m)$ satisfies the differential equation

$$
\frac{d}{d\tau}T_\tau(\Omega_n|\Omega_m) = QT_\tau(\Omega_n|\Omega_m)
$$

$$
Q = (3\tau_r)^{-1}\begin{bmatrix} -2 & 1 & 1 \\ 1 & -2 & 1 \\ 1 & 1 & -2 \end{bmatrix},
\tag{A38}
$$

50

so that the transition density is given by

$$T_\tau(\Omega_n|\Omega_m) = \frac{1}{3} + \exp(-\tau/\tau_r)\left(\delta_{mn} - \frac{1}{3}\right).\tag{A39}$$

Equations A36 and A37 are then readily evaluated leading to the correlations functions indiacted by 144.

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