COMMUTATOR-BASED $(A)[X]_n$ $(SU(2)\times\mathcal{S}_n)$ NMR CLUSTER SYSTEMS: ESTABLISHMENT OF THE UNIVERSALITY OF $[\hat{n}](\mathcal{S}_n)$ SALIENTS AND CONSTRAINTS ON $\hat{\phi}^1_{\pm1}(1.1)$ POLARISATIONS TO THE $[\hat{1}^n]$ SALIENT: PERMUTATIONAL SPIN SYMMETRY(PSS) WITHIN NMR SPIN DYNAMICS – AN ANALYTIC VIEW

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Dedicated to Professor Josef Paldus on the happy occasion of his 70th birthday and in appreciation of his warm friendship.

Analytic $SU(2)\times\mathcal{S}_n$ dual tensorial (DT) spin dynamics over uniform NMR spins is invoked in examining the modern quantum basis for the universal non-observability rule which governs dominant intracluster $J_{XX'}$ couplings of $(A)[X]_n$ NMR systems as a specific form of (abstract) permutational spin symmetry (PSS) with well defined properties on spin-alone space. This is shown to be linked to DT constraints that apply to the cross-product $\hat{\phi}^1_{\pm1}(1.1)$ polarisation development i.e., as being confined to $[\hat{1}^n](\mathcal{S}_n)$ (Liouvillian) salient, with the existence of $[\hat{n}]$ (rotating frame) null subspaces. Both these arise within the spin dynamics of $(A)[X]_2$ spin systems (or subsystems thereof) within (a hierarchy of) dominant $J_{XX'}$ governing the internal $\hat{\mathbf{L}}^{(0)}$; such spin systems provide analytic sequels to comparative spin dynamics studies of XX′ PSS and AX broken-PSS systems in a Liouvillian coupled tensorial basis formalism, since both draw on (Sanctuary B. C.: *Mol. Phys.* **1985**, *55*, 1017), and on the realisation that proper PSS over a (uniform) spin-space $\hat{\mathbf{L}}^{(0)} = [\hat{\mathbf{H}}^{(0)},.]$ zeroth-order Liouvillian and its internal (hierarchical subsets of) $J_{XX'}$ (Temme F. P.: *J. Mol. Struct. (THEOCHEM)* **2002**, *547*, 153) i.e., for abstract $\mathcal{S}_n \downarrow \mathcal{G}$ group embeddings. The present work also examines the general irrep-structure of DT spin symmetries for the extent of unit-character irreps and the role of $\mathcal{S}_n \supset \mathcal{S}_{n-1} \supset .. \supset [2](\mathcal{S}_2)$ group chains in defining the $\mathcal{S}_n$ multiple invariants under democratic recoupling of PSS of uniform spin systems. As group measures, these properties apply to both $(A)[X]_n$ and $[AX]_n$ PSS symmetries, with the invariant cardinality $|SI|^{(n)}$ being related to time-reversal invariance (TRI) and its inherent democratic recoupling (DR) over Weyl $(\mathbf{I}\bullet\mathbf{I})$ pairs. For $[X]_{2n}$ uniform spin clusters, $|SI|^{(2n)}$ is best derived via n-fold polyhedral combinatorics of the underlying DR (Temme F. P.: *Proc. R. Soc. London, Ser. A* **2005**, *461*, 321) i.e., as an augmented post-Weyl view of the essential role of TRI in (group) invariant cardinality, with the $\mathcal{S}_n$-invariants represented by certain $\mathcal{S}_n$ subduction properties.

Keywords: NMR spin dynamics theory; Democratic recoupling; Permutation spin symmetry; Nuclear magnetic resonance; Time-reversal invariance.

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The NMR literature allows one to distinguish clearly between effects derived from abstract (uniform) spin-space, zeroth-order Liouvillian(s) for the (initial) NMR evolution process under permutational spin symmetry (PSS)[1–6], as compared to those based on particle (or molecular) quantum physics-induced parity, or other residual invariance effects[7], such as time-reversal invariance (TRI), **T**. Even for NMR ensemble spin systems which only exhibit broken-permutational spin symmetry (B-PSS)[7] (or for the case of a single higher-**I** spin[8–10]), the independent parity invariance **P** (distinct from PSS) is still of considerable conceptual value. It is especially important to note here that the PSS spin symmetry of (liquid state, or nematic state) NMR (i.e., as an automorphic $\mathcal{S}_n \downarrow \mathcal{G}$ spin symmetry[1] on an abstract spin space[2]) derives exclusively from the zeroth-order (Hamiltonian or Liouvillian) structure[2,6], and is based specifically on the $\mathcal{S}_n \supset \mathcal{S}_{n-1} \supset .. \supset [2](\mathcal{S}_2)$ subgroup (subduction) chains of the spin space, rather than any of the orthogonal chain processes typical of (vibrational, or electronic) spectroscopic phenomena. The theory of PSS applied to uniform spin NMR ensembles specifically excludes the latter type of group subduction – for reasons discussed later.

For analogous isochronous NMR systems associated with broken-permutational spin symmetry (B-PSS), the residual particle symmetries (e.g., parity as derived from the known independence of the C**P**, C**PT** invariances) are important properties[7]. Both **P** parity and **T** TRI properties of (uniform ensemble) NMR systems naturally contribute to the structure of any tensorial basis formalism, e.g. those given in refs[7–12]. Both $\{|IM.\rangle$ and $\{|kqv\rangle\rangle$ quantal basis formalisms allow one to recognise the parity aspects of even/odd tensorial rank labelling, whereas (by comparison) the presence of TRI [13], '**T**' of C**PT** above, in NMR arises indirectly. Its quantal effect may be realised from the pairwise permutational exchange properties of the $(\mathbf{I} \bullet \mathbf{I})_\mathbf{i}(\mathbf{I} \bullet \mathbf{I})_\mathbf{j}(..)_\mathbf{k}..$ Weyl–Corio bracket algebras[14]. For simple (non-uniform) spin systems, its linear (Weyl) bracket chain defines the system-defined independant cardinality of the (multiple) scalar invariants (see the Appendix for more details on questions of the inter-collations of (Weyl **T**- and bracket algebra)-defined independent invariant cardinalities and the $\mathcal{S}_n$ representational subgroup chains[17,19]), and hence the algebraic completeness of auxilliary labelling associated with certain (Liouvillian) dual projective mappings. These ancillary label properties (or the equivalent graph invariants in other types of systems) are explicit labels[15] only for Liouville space superboson mappings[15]. Because of their derivation, group invariants constitute (Lie algebra) group measures[16] associated with the $SU(2) \times \mathcal{S}_n$ dual group maps. By contrast the simple Hilbert space boson mapping formalisms (applicable to electronic structure problems), the $\mathcal{S}_n$ invariants are simply implicit variables[17,18] of the mapping. A fuller appreciation of the quantum physics underlying NMR evolution, or mixed evolution/(quadrupolar) relaxation processes requires the use of some (augmented) tensorial form[4,8–12] of the quantum-Liouville equation (Eq. (*1*) below), with the use of some particular initial condition for $\phi_q^k(v)$ ($t = 0$) (e.g. for various types of (higher-**I**) spin systems), in order to adequately describe the nature of the NMR spin dynamics[8–10] over a sequence of pulses. As classic area of spin dynamics, these sequences (whether for solid-state[23] or liquid-state NMR applications) arise from detailed 'time-reversal or phase' information which is quite distinct from the TRI properties described below. For its contextual interest beyond the present application(s), it is noted theories solid-state spin ensembles represents an extensive field involving 3-space (graphical) lattice-based spin-interaction networks[24].

The tensorial formalisms introduced by Sanctuary, Halstead and their co-workers[9–11] in the mid-1980s express the density operator $\rho[t]$ in terms of a set of expectation values associated with the full set of tensorial bases[10]. Thus the quantum Liouville equation (here including the relaxation term and given in a suitable ($\hat{\phi}_q^k(v)$) rotating frame with integer k ranks) takes the dynamical form:

$$-\mathrm{i}\hbar\hat{\phi}^{\bullet} = \{\hat{\hat{\mathcal{L}}} - \mathrm{i}\hat{\hat{\mathcal{R}}}\}\hat{\phi}(0) \tag{1}$$

with $\hat{\phi}_{\pm q}^k$ polarisation being the rotating-frame expectation value $\left\langle\langle T_q^k(v)\rangle\right\rangle_{\text{rot.frame}}$ derived from

$$\hat{\phi}_q^k \equiv \left\langle\langle T_q^k\rangle\right\rangle_{\text{rot.frame}} = \mathrm{Tr}\,\{\hat{\rho}[t]T^{kq}(v)\}, \quad k \text{ integer} \tag{2}$$

where $\hat{\rho}[t]$ is the density operator associated with the Schrödinger formalism, and $\{T^{kq}(v)\} \equiv \{|\,kq(v)\rangle\rangle\}$ represents the complete Liouville space basis with its full set of integer rank k, projection q, components, together with various v ancilliary ((DR-based) v invariant, or other recoupling) parameters. Certain additional details of the formalism, including their various transformational properties, are included in Appendix to help orientate the reader who is more familiar with $\{|IM\rangle\langle IM'|\}$ product formalism of NMR utilised in treating simple non-uniform or isochronous spin systems[20]. A fuller description of interrelationships of product spin formalisms and tensorial basis formalism may found in a 1986 work due to Sanctuary[11b].

ENSEMBLE NMR SPIN DYNAMICS VIA $SU(2)\times\mathcal{S}_n$ TENSORIAL SETS: ANALYTIC VIEW

In terms of the cross-product polarisations $\phi^1_{\pm1}(k'_1 k'_2)$ as (notational) NMR observables, the first analytic description of the initial evolution/development stage for the AX spin system[11] was given in 1985; an outline of the notation and methods utilised, and some of the results obtained, have been summarised for convenience below, and for completeness in Appendix. These analytic results have been augmented and reformulated in a specialised way subsequently to describe the PSS-based identical two-spin system[12]. It is the form of these final analytic structures of XX′ system spin dynamics which allows one a fuller understanding of the quantum-based group theoretic nature of $[X]_n$, or $(A)[X]_n$, PSS spin system (sub)spectra in general. In turn, this leads to a systematic differentiation of the above systems from the dynamics of the contrasting B-PSS, or isochronous B-PSS [7,20] NMR systems, in which the intracluster spin coupling is no longer the dominant ensemble interaction determining $\hat{\mathbf{L}}^{(0)}$. In addition, the XX′ analytic form of ref.[12] highlights the importance of the relationships between PSS, in the form of its Liouvillian properties, and various earlier NMR commutator properties[5,6] of Hilbert space-based realisations of nuclear spin PSS. Hence a fuller understanding of the origins of a universal long-established quantum physics property inherent in dominant intracluster interactions of the $(A)[X]_n$ type of uniform spin system[6,21] is obtained as it concerns the non-observability of dominant intracluster $J_{XX'}$ (homonuclear) coupling(s) in $(A)[X]_n$ PSS spin systems. This is derived here in a modern analytic spin dynamics formalism, which draws on various aspects of representational theory and the simpler aspects of (superboson) dual mappings inherent in quantum-Liouville formalisms.

One final introductory remark is called for here for its pertinent to various applications. This concerns the use of Liouville spin space-derived representations in specific applications (e.g., PSS symmetry breaking) and the importance of retaining all the conserved spin particle and PSS symmetry properties, including $\mathcal{S}_n$ invariants, for the clarity which they impart to the final analytic form(s) of NMR observables. The value of such general approaches has been widely demonstrated in applications given the modern NMR, and/or NQR, literature, e.g., within the works of Happer[8], Krishnan et al.[9], Sanctuary and Halstead[10], or more recently Bain[22] and others. Such tensorial formalisms retaining **P**, **T** invariance properties then yield an invaluable block-factored $\mathcal{L}$ representational matrix form, which gives the simplest possible view of the resultant analytic spin dynamics. These views imply that all the conserved invariances, including C**P**, C**PT**, are retained as well as the uniform spin system's scalar invariants (under PSS) whose cardinality derives from more specific time-reversal considerations[14], the subject of recent work[15] on general 2*n*-fold (uniform) identical spin ensembles.

XX′ = $[X]_2$ IDENTICAL SPIN LIMITS AS A MODEL FOR WIDER PSS NMR SPIN SYSTEMS $[X]_n$

On comparing and contrasting the NMR spin dynamics for two spins under the two possible distinct limits, i.e. of being distinct, or strongly coupled identical resonance frequency spins within the background material given in ref.[11] (and the spin dynamics relationships between tensorial and product formalisms, given in Appendix, one is in a position to develop models for PSS and B-PSS spin symmetries, utilising a common Liouvillian for the two (and higher *n*-fold) identical spin model systems which reduce to the form for AX case of

$$\mathcal{L}/\hbar = [\mathrm{i}w_{01}\, T^{10}(10) + \mathrm{i}w_{02}\, T^{10}(01) + \sqrt{3/2}\, J\, T^{0}(11), \quad]_{-}$$

for the specialised identical resonance frequency two-spin XX′ system case from the above equation to

$$\mathcal{L}/\hbar = [\mathrm{i}\sqrt{2}\, w T^{10}([2])(\mathcal{S}_2) + \sqrt{3/2}\, J\, T^{0}(11), \quad]_{-} \tag{3}$$

with the Liouvillian component $T^{1q}([\tilde{2}]) = \{T^{1q}(10) + T^{1q}(01)\}/\sqrt{2}$ and where w is now the mean resonance frequency. Hence it follows that

$$[\mathrm{i}\sqrt{n}\, w T^{10}([n]) + \sum_{i,j:i\le j} \sqrt{3/2}\, J_{ij}\, T^{0}(0.1_i 1_j.0), \quad]_{-}$$

is the general form for Liouvillian of all the wider uniform/identical *n*-fold strongly intracluster-coupled spin ensemble systems.

XX′ as a Model for More General $[X]_n$, $(A[X]_n)$ Spin Systems – from AX

The alternative to the Sanctuary analytic formalism of ref.[11], summarised in Appendix, is the *XX′* limit, in which w_D eventually vanishes. This provides for an additional partial uncoupled problem over the $\phi^1_{\pm1}([2])$, $\phi^2_{\pm1}([11])$, and $\phi^1_{\pm1}([1^2])$, $\phi^1_{\pm1}([11])$ coupled polarisation subsets[12], as expectation values of specific (spin-alone) tensorial components. This arises once certain row/column additions/subtraction and related transformations are invoked and suitable rotating frame transformations adopted. One then finds (for ϕ^k_qs correlated to either primary tensors or unnormalised dual tensors) that

$$(\mathrm{d}/\mathrm{d}t)\begin{pmatrix} (1/\sqrt{2})\hat{\phi}^1_1([\tilde{2}])[t] \\ \hat{\phi}^2_1(11[\tilde{2}])[t] \\ \hat{\phi}^1_1(11[\tilde{1}^2])[t] \\ (1/\sqrt{2})\hat{\phi}^1_1([\tilde{1}^2])[t] \end{pmatrix} =$$

$$= \mathrm{i}\begin{pmatrix} 0 & 0 & 0 & \pm 2w_\mathrm{D} \\ 0 & 0 & w_\mathrm{D} & 0 \\ 0 & w_\mathrm{D} & 0 & \mathrm{i}\sqrt{2}J \\ \pm 2w_\mathrm{D} & 0 & -\mathrm{i}J/\sqrt{2} & 0 \end{pmatrix}\begin{pmatrix} (1/\sqrt{2})\hat{\phi}^1_1([\tilde{2}])[0] \\ \hat{\phi}^2_1(11[\tilde{2}])[0] \\ \hat{\phi}^1_1(11[\tilde{1}^2])[0] \\ (1/\sqrt{2})\hat{\phi}^1_1([\tilde{1}^2])[0] \end{pmatrix}. \quad (4)$$

Clearly from Eq. (*5*), $\hat{\phi}^1_1([\tilde{2}])[t]$ becomes a constant of motion once the vanishing w_D limit is imposed. In consequence, the $[\tilde{2}](\mathcal{S}_2)$ subspace then represents a null irrep-salient for the PSS-based XX′ uniform identical spin system; one pair of ϕ^k_q polarisations remains coupled however, as we pointed out in our earlier discussions on strong intra-coupled PSS systems[12]. In contrast to that work, here we have adopted a w_D skew-diagonal representational form for the coupled matrix, prior to imposing the limit condition. From Eq. (*5*), the single quantum eigenfrequencies (labelled by their $[\tilde{\lambda}]$ salient and tensorial *k* rank here as sub/superscripts) become

$$\{\lambda_i\} = \{0\}^{k=1}_{[\tilde{2}]}, \quad \{0\}^{k=2}_{[\tilde{2}]}, \quad \{\pm J\}^{k=1}_{[\tilde{1}^2]}. \quad (5)$$

It is of some further interest to consider certain formal analytic solutions for $[X]_2$ PSS spin dynamics, e.g.

$$\hat{\phi}^1_q([\tilde{2}])[t] = 0 \quad (6)$$

and

$$\hat{\phi}_q^1([\tilde{1}^2])[t] \sim J_{XX'} \int_0^t \exp \mathrm{i}(t - t')qw\, \phi_q^1(11)[t']\, \mathrm{d}t' \qquad (7)$$

for the full identical two spin case in its vanishing w_D limit. It is these two equations which best serve to demonstrate the nature of $J_{\mathrm{XX'}}$ intracluster coupling. Clearly, $J_{\mathrm{XX'}}$ interaction lies exclusively within the $[\hat{1}^2]$ (antisymmetric) salient and is thus not physically observable, i.e., on account of the NMR observable (for the most general $[X]_n$ (etc.) case) being the Liouville space ensemble averages:

$$\left\langle \langle F_{-1}^1 \rangle \right\rangle = \left\langle \langle T_{-1}^1 [\tilde{n}](\mathcal{S}_n) \rangle \right\rangle . \qquad (8)$$

For the specific PSS two-spin system discussed here, this reduces to $\left\langle \langle T_{-1}^1 [\tilde{2}] \rangle \right\rangle$. Because $\hat{\phi}_{\pm 1}^1([\tilde{1}^2])[t = 0]$ is not a physically accessible initial polarisation associated with any known, or conceivable, specific pulse-sequence in to-day's NMR, this conclusion holds also for the full spin dynamics, Eqs (*5*)–(*7*) above. The generalised $(A)[X]_n$ system spin dynamics allows for the retention of null $[\tilde{n}]$, and inaccessible $[\tilde{1}^n]$ salients, as specific properties of the $(A)[X]_n$ focussed on here as compared to $[AX]_n$ totally bipart uniform spin systems.

$SU(2) \times \mathcal{S}_n$ IRREPS: PERTINENCE AND EXTENT OF $\chi_{1^n}^{[\lambda]}$ ABELIAN CHARACTERS IN $(A)[X]_n$ SPIN DYNAMICS

In addition, a brief consideration of the symmetric group irrep structural hierarchy (where the mathematical symbols {.} and | refer respectively to 'set' and 'for which'; both are invoked here and below. Details of general hooklength rule for the standard evaluation of $\chi_{1^n}^{[\lambda]}$ permutational group character(s) can be found in earlier work[15] and in the standard $\mathcal{S}_n$-algorithm texts cited therein) associated with $SU(m) \times \mathcal{S}_n$ dual algebras is given as it is invaluable in defining the following irrep (char) sets:

$$\{[2]; [11]\};$$

$$\left\{ [3]; [21]_{\mathrm{SA}}; [1^3] \,\middle|\, \chi_{1^3}^{[21]} = 2 \right\} (\mathcal{S}_3) \qquad (9)$$

$$\left\{[4];[31],[2^2]_{SA};[211],[1^4]\,\middle|\,\chi^{[31]}_{1^4}=\chi^{[211]}_{1^4}=3;\chi^{[2^2]}_{1^4}=2\right\}(\mathcal{S}_4) \tag{10}$$

and eventually under $\mathcal{S}_{12}$:

$$\left\{[12],[11,1][10,2],..;\{[621^4]_{SA}.,[4422]_{SA}\};..[21^{10}],[1^{12}]\,\middle|\,\middle|\text{ only }\chi^{[12]},\chi^{[1^{12}]}\text{ unit chars}\right\}(\mathcal{S}_{12})\;. \tag{11}$$

In the general context of hierarchical structures, this essentially demonstrates that it is only the $[\tilde{n}]$ and $[\tilde{1}^n]$ irreps of the n-indexed symmetric group which exhibit (quasi-Abelian) unit characters. This in turn implies that the only meanful spin dynamics associated with general indexed identical spin systems likewise occurs in these salients only, with the rotating frame null space result being general for all totally symmetric $[\tilde{n}]$ irreps originating in some corresponding $[X]_n$ system, or in a subspectrum of an $A[X]_n$ PSS-based spin system. Two further comments are called for at this point. The first of these comments concerns the irrep sets associated with higher-indexed permutation groups and their related $SU(m)\times\mathcal{S}_n$ dual groups. These are governed by the independent cardinality of $\mathcal{S}_n$ group invariants, a property that, irrespective of the (original) SU(m) spins involved, is realised in terms of the $SU(2)\times\mathcal{S}_n$ duality and its associated time-reversal invariance (**T**) properties[14,15]. The wider significance of this fact has been discussed in detail elsewhere[15].

On account of this earlier extensive treatment of the topic in the context of the polyhedral-based approach to democratic recoupling[15], it is only briefly mentioned here in the next section, now in the context of (superboson) quasiparticle mapping over Liouvillian carrier space[15b] for the completeness of $\{D^k(\tilde{\mathbf{U}})\times\tilde{\Gamma}^{[\tilde{\lambda}]}(v)(\mathcal{P})\}$ dual algebra. Our second point concerns the value of specific applications of the more general tensorial methods for 3-space-based spectroscopies, as reviewed in the monograph by Silver[25], and their contrasts with alternative group theoretical methods. These constitute only one part of such theories, as there exist certain contrasting mutually exclusive roles for tensorial techniques[18b] and Lie algebraic approaches[26] to the (mathematical) structure of group theory itself (here the work of Kirillov[16] of the Russian school provides an invaluable in-depth reference guide to Lie algebra and its methods). Some appreciation of the nature of these methods is useful to any in-depth view of the role of group theory in quantum mechanics; Tung's rather concise text[24] illustrates the nature of group structure from a Lie algebraic (or structure factor) point of view, and provides a useful brief introduction to the role of such methods in quantum physics. Clearly the two methods complement each other, with the (dual) tensorial aspects of group theory (largely based on methods set out in refs[17–19]) predominantly being utilised here in defining the NMR PSS of uniform spin ensembles. (The wreath-product, despite in importance in other area of spectroscopy[27], is not pertinent to abstract PSS of NMR; it occurs then only in specialised applications e.g., quantum rotational tunnelling NMR problems.)

'ALGEBRAIC COMPLETENESS' IN DUAL MAPS: ROLE OF 'T'-BASED INVARIANTS AND $\mathcal{S}_n$ SUBGROUPS

Further aspects of the theoretical quasiparticle quantum physics from 1970–mid-1980s, as set out in work of Biedenharn and Louck[18], are of some interest here in the context of algebraic completeness of the $SU(2) \times \mathcal{S}_n$-defined basis sets, where now the latter are of integer rank as Liouville space forms. From the form of dual unitary-symmetric group irrep sets for j half-integer rank here with λ of a bipartite form

$$\left\{ D^j(\mathbf{U}) \times \Gamma^{[\lambda]}(\mathbf{P}) \mid \mathbf{U} \in SU(2); \mathbf{P} \in \mathcal{S}_n \right\} \tag{12}$$

as a Hilbert carrier space-derived property so that the standard Hilbert quasiparticle boson mapping[18] (given below) follows directly. In Hilbert space, the unitary and $\mathcal{S}_n$ projection operators act on a simple carrier space $\mathbb{H}$, so that the dual mapping is simply:

$$\mathbf{U} \times \mathbf{P} : \mathbb{H} \to \mathbb{H} \left\{ D^j(\mathbf{U}) \times \Gamma^{[\lambda]}(\mathbf{P}) \mid \mathbf{U} \in SU(2); \mathbf{P} \in \mathcal{S}_n \right\} ; \tag{13}$$

clearly this mapping property highlights two concepts: the simple-reducibility (SR) associated with the SU(2) group, and the completeness of the dual algebra, or its associated irrep set. In contrast for the equivalent Liouvillian dual tensors over a superboson (quasiparticle)-based carrier space[15], it is essential to include certain explicit group invariants. These additional labels allows the retention of the Liouvillian simple reducibility (SR) properties for the integer-rank irrep set in the corresponding dual mapping

$$\tilde{\mathbf{U}} \times \tilde{\mathcal{P}} :$$
$$\tilde{\mathbb{H}} \to \tilde{\mathbb{H}} \left\{ D^k(\tilde{\mathbf{U}}) \times \tilde{\Gamma}^{[\tilde{\lambda}]}(v)(\mathcal{P}) \mid \tilde{\mathbf{U}} \in SU(2), k \text{ integer}; \ \tilde{\Gamma}^{[\tilde{\lambda}]}(v)(\mathcal{P}) \in \mathcal{S}_n , v \text{ invariant} \right\} \tag{14}$$

now with $[\tilde{\lambda}](\mathcal{S}_n)$ being of some appropriate quadra-partite form. These $[\tilde{\lambda}]$s are obtained from Hilbert space irreps, via an allowed direct product (DP) formation (see below). One notes that it is this type of structure which provides the proper general interrelationship between Hilbert and Liouville spaces. The presence of the $\mathcal{S}_n$ invariants as (v) explicit carrier subspace labels ensures that

$$\tilde{\mathbb{H}} \equiv \sum_{(v)} \tilde{\mathbb{H}}_{(v)} \tag{15}$$

where, in the context of Lie algebra, the set of v constitute formal group measures[16], a requisite property for the validity of the DP formation mentioned above. One further important concept is associated with these invariants, namely that they restore the necessary SR to the dual irrep (sub)sets, since the projective action is now on an appropriate $\tilde{\mathbb{H}}_{(v)}$ carrier subspace[15,28,29]. As a corollory to this DP interrelationship of Liouville and Hilbert space, it follows[4] that the respective $\mathcal{S}_n$ projection operators $\mathcal{P}_\mu$, and for Hilbert space $\mathbf{P}_{\mu'}$ act over the tensorial set, to give

$$\mathcal{P}_{[\tilde{\lambda}]}(\mathcal{S}_n) T^{kq}(v) \equiv \sum_{\text{for } \lambda', \lambda'' \text{ of } [\tilde{\lambda}] = \lambda' \otimes \lambda''} \mathbf{P}_{\lambda'} T^{kq}(v)\, \mathbf{P}^\dagger_{\lambda''} \equiv \{ T^{kq}(v : [\tilde{\lambda}]) \} \tag{16}$$

where the analogous $\tilde{\mathcal{C}}_\mu$, C_μ (Liouville, Hilbert) class-operators of the group algebra are defined by standard tensorial forms[2,4], via the relationship

$$\mathrm{Tr}\, \tilde{\mathcal{C}}_\mu T^{kq}(v) = \mathrm{Tr}\, C_\mu T^{kq}(v) C^\dagger_\mu . \tag{17}$$

In addition, the $n_{[\tilde{\lambda}]} = Tr\ \mathcal{P}_{[\tilde{\lambda}]}$ Liouvillian properties based on Eq. (*16*) follow directly from the group algebra. Naturally these yield results which are identical to those derived via the trace $\mathcal{P}_{[\tilde{\lambda}]}$ forms and explicit DP formation (as in Eq. (*16*)). Tabulations of the Liouville space dual irreps follow directly from these properties, (i.e.) for two spin –1/2, as in Table 2 of ref.[2], and the corresponding two spin-one dual tensorial symmetrisation also reported therein. More extensive tabulations of the dual irreps associated with the $[A]_4$, $[AX]_4$ uniform spin one-half systems are known to span a range of inter-related automorphic (embedded) symmetries[4,30], with the automorphic subgroups (therein) for NMR problems defined in terms of the types of hierarchies associated with the distinct $J_{XX'}$ intracluster interaction subsets of the zeroth-Liouvillian, or $[\hat{\mathbf{H}}^{(0)},.]_-$. The value of the (super) quasiparticle view of Liouville space-based carrier subspace properties (with the specific exception of (*v*) invariants being $\mathcal{S}_n$ group measures) have been discussed at some length in earlier work of ours on invariants, SR and $SU(2)\times\mathcal{S}_n$ mappings[15,28,29] and the determinacy of $\mathcal{S}_n \downarrow \mathcal{G}$ group embeddings[30], from 1990s. Group/subgroup chain subductions are invaluable also in realising the $\mathcal{S}_n$ invariants of NMR. These chains help to explain why the automorphic PSS symmetries of NMR are related to $\mathcal{S}_n$-based democratic recoupling, and also precise how they differ from 3-space symmetries, typical of conventional optical spectroscopies and electronic properties. Clearly, PSS symmetries are governed by the symmetric groups within the general permutational subgroup subduction scheme

$$\mathcal{S}_n \supset \mathcal{S}_{n-1} \supset \ldots \supset \mathcal{S}_2 ; \qquad (18)$$

on realising the full set of specific subgroup irreps as routes within the chain scheme that map onto $[2]\mathcal{S}_2$ (after ideas given in the particle symmetry monograph due to Chen[17]) one has a convenient form that represent the (group) scalar invariants. On treating this process as a form of enumeration, one obtains the (independent) cardinality of the corresponding $\mathcal{S}_n$ from the number of such routes, so that the three- to five-fold identical $[A]_n$ NMR spin systems, and/or *n*-indexed $\mathcal{S}_n$ groups, correspond respectively to the irrep subgroup chain sets (i.e., ending on $[2]\mathcal{S}_2$):

$$[21](\mathcal{S}_3) \supset [2] ; \qquad (19)$$

$$[31] \supset [3] \supset [2]; \quad [31](\mathcal{S}_4) \supset [21] \supset [2]; \quad [22] \supset [21] \supset [2] \qquad (20)$$

and finally for $[A]_5(\mathcal{S}_5)$, the set of subgroup chain-based irreps:

$$[41] \supset [4] \supset [3] \supset [2]$$

$$[41] \supset [31] \supset [3] \supset [2]$$

$$[41] \supset [31] \supset [21] \supset [2]$$

$$(21)$$

$$[32] \supset [31] \supset [3] \supset [2]$$

$$[32] \supset [22] \supset [21] \supset [2]$$

$$[311]_{SA} \supset [31] \supset [3] \supset [2] \,.$$

Specifically the extent of these $\mathcal{S}_n \supset \mathcal{S}_{n-1} \supset .. \supset \mathcal{S}_2$ chains of component subgroup irreps suggest an enumerative method for the corresponding $\mathcal{S}_n$ group invariant cardinalities; for the examples given above, one finds that $|SI|^{(n)} \equiv$ 1:3:6, respectively. For higher indexed originating $\mathcal{S}_n$ groups, the number of (independant) group invariants based on $p \leq 4$ [λ] subgroup irrep chains for (all) [λ] prior to/including $[\lambda_{SA}](\mathcal{S}_n)$ could well be over-determined.

General $2n$ index evaluation of these cardinalities of the $\mathcal{S}_n$ invariants[15a,15c] necessarily draws on some earlier ideas concerned with the nature of democratic recoupling and also with the related question of analytic indeterminacy inherent in all systems governed by the multiple invariants of democratic recoupling[18c], exhibiting high levels of degeneracy. Indeed, a central role for **T** time-reversal invariance in physics lies in its defining these $|SI|^{(2n)}$ invariant cardinalities, i.e., via a polyhedral combinatorial formalisms augmenting[15] the earlier linear recoupled, bracket algebraic theory, originally due to Weyl[14b], discussed at some length elsewhere[15]. By contrast, it is well established that conventional spectroscopies and electronic angular momentum-based properties, as in (e.g.) the Lynden-Bells' presentation[31] and Atiyah and Sutcliffe's discussion[32] of the $SO(3) \times \mathcal{S}_n$ dual group, the role of the symmetric group does not dominate the treatment, as it does for spin-alone space of NMR dual groups. Such (non-NMR) systems are associated with various distinctive $\mathcal{O}_n$ orthogonal group chain subduction processes. This distinction is fundamental to a proper understanding of the difference of 3-space symmetries from the various group theoretic aspects of abstract automorphic PSS based on democratic recoupling, discussed here. It arises on noting, that while

$$SU(2) \leftrightarrow SO(3) \tag{22}$$

constitutes a 2:1 homomorphism, no analogous (homo)morphism exists for any of the multiple $SU(2) \otimes .. \otimes SU(2)$ structures. Indeed, it is known that

$$SU(2) \otimes SU(2) \rightarrow \mathcal{G}|SO(5) \supset \mathcal{G}\} \,. \tag{23}$$

As a consequence of this fact, the orthogonal group chains and (linear) graph theory of conventional spectroscopies in general do not apply to the extensive multiple identical (uniform) spin systems of NMR, or to their recoupling – a point not widely recognised in some of the earlier work on NMR spin systems[10]. This also brings into question the fuller generality of the earlier conventional $|(\otimes D^0(\mathbf{U}))|^n$ techniques, as utilised (e.g.) by Corio[14] to derive the invariant cardinality for modest-indexed multispin systems under PSS. (Clearly these remarks derive from (e.g.) Wybourne's 1976 monograph[19] which sets out the importance of the $\mathcal{GL}_n$ subgroup structure, of which $\mathcal{S}_n$ group forms a natural part.)

CONCLUDING REMARKS

The theoretic spin dynamical significance of certain established dominant intra-cluster interaction-based commutator relationships inherent in the PSS-based $(A)[X]_2$ as being typical of $(A)[X]_n$ spin systems (or their $A[X]_n$ subspectra) has been derived from a tensorial analytic treatment of a XX′ model system (cf. to the AX system's J_{AX}-based $\phi^1_{\pm 1}(1.1)$ polarisation transfers[11]), and from the inherent limitations of the analogous (non-degenerate) unit $\chi^{[\lambda]}_{1^n}(\mathcal{S}_n)$ characters of the $\mathcal{S}_n$ algebra, with these being restricted to the totally-symmetric $[n]$, or the totally-antisymmetric $[1^n]$ irreps. The value of the Liouville-space tensorial formalism adopted here is seen in the clarity of its analytic quantal physics for these specific $(A)[X]_n$ system forms, as distinct from the $[AX]_n$ systems, in which the observable NMR polarisations under PSS are restricted to a (rotating frame-based) **null** space, whilst the dominant $J_{\mathrm{XX'}:\mathrm{intracl.}}$ and cross-product-based algebra(s) over $\{\phi^1_q([1n]), \phi^1_q(11), ..\}$ are all confined to the inaccessible antisymmetric $[1^n]$ salient(s). In addition, the C**P**, C**PT** NMR residual invariance features are distinguishable from the $\hat{\mathcal{L}}^{(0)}$-based, spin space PSS symmetry features.

For the higher n-indexed $(A)[X]_n$ systems and their spin dynamics, the underlying roles of $\mathcal{S}_n \supset \mathcal{S}_{n-1} \supset .. \supset [2]\mathcal{S}_2$ chains, and their associated democratic recoupling, characterising these multi-invariant spin systems raises the question of the existence of a limit to the analytic determinacy of dual PSS-based spin dynamics. Such concerns are comparable to the modest analytic determinacy limit (beyond the specialised Jacobian forms of ref.[33]) recognised by Galbraith[34], in the context of orthogonal subgroup chain-based democratic recoupling associated with conventional (non-NMR) degenerate spectroscopic systems.

An important role of explicit Liouvillian ancilliary $\mathcal{S}_n$ invariant labelling, i.e., now in terms of $\mathcal{S}_n \supset \mathcal{S}_{n-1} \supset .. \supset [2](\mathcal{S}_2)$ symmetric group (not orthogonal group) chains[17], is that of retaining the simple reducibility (SR) properties of Liouvillian $SU(2) \times \mathcal{S}_n$ dual group algebras, whose $\{D^k(\tilde{\mathbf{U}}) \times \tilde{\Gamma}^{[\lambda]}(v)(\mathcal{P})\}$ set-completeness (for k integer and $[\tilde{\lambda}]$ quadra-partite forms) is demonstrated by nature of $\tilde{\mathbf{U}} \times \mathcal{P}$ (map) actions on $\tilde{\mathbb{H}}$ quasiparticle carrier space defined by superboson mapping[15b,27]. The direct product structure of such Liouville space-based irreps is seen as a fundamental consequence of the $v(\mathcal{S}_n)$ group invariants, which are invaluable in labelling the (augmented) carrier subspaces-based mappings and retaining SR, being group measures in a Lie algebraic sense, described by Kirillov[16]. The conceptual significance of this has been discussed elsewhere[15a,15c]. All of these presentations constitute sequels to our earlier reviews[30] of the theoretic basis of maximal $\mathcal{S}_n \downarrow \mathcal{G}$ mathematical determinacy for NMR-related automorphic group embeddings. A useful criterion exists in the independence of all (bijective) mappings (i.e., prior to, and including, the λ_{SA} self-associate irrep embedding(s)[30]) for $SU(m) \times \mathcal{S}_n \downarrow \mathcal{G}$ maps. This was shown to be both a necessary and sufficient criterion. This is clearly a significant augmentation of earlier theories of group embedding; it lies well beyond the limited known criteria associated with Cayley's theorem based on $SU(2) \times \mathcal{S}_n$ properties. From the nature of these $\mathcal{S}_n \downarrow \mathcal{G}$ group embeddings[30], clearly PSS is properly an automorphic symmetry, as originally defined in the early 1980s by Balasubramanian[1].

The reader will readily recognise also that the dual symmetries of NMR (derived from identical nature of spins within zeroth-order Liouvillians) are necessarily symmetric-subgroup chain-based properties[2,15,29] (as shown above), not orthogonal subgroup-based entities as are pertinent to conventional spectroscopies and EPR-studies of crystals. Aside from I, or k rank, parity features, it should be appreciated that 3-space aspects (apart from in respect of the established role of parity) has absolutely no role in NMR spin dynamics. Finally it should be noted here that the original Balasubramanian (permutational network) views of the nature of automorphic (spin) symmetry[1] for the PSS of NMR and $\mathcal{S}_n \supset \mathcal{S}_{n-1} \supset .. \supset \mathcal{S}_2$ leads to the need for corrections to the (orthogonal group-based) notation of (the late) Corio[14a], for group theoretical reasons indicated. The wider importance of tensor manifolds in physics may be seen (e.g.) in the text due to Wasserman[35]. The correlation of (superboson (as a pattern algebra)) mappings and their sign-based structure to Lie algebra has been given elsewhere[15], with the details of the closed superboson algebras presented in our early 1990s work[15b].

As a final pertinent point of experimental NMR interest, it is useful to stress here that (despite (erroneous) reports in the literature to the contrary) neither quadrupolar[21] or simple dipolar[36] **R**-relaxation terms of Eq. (*1*) provide a suitable theoretic mechanism for (spin-alone space) automorphic PSS symmetry breaking. Any observed departure from the universal dominant $J_{XX'}$ non-observation rule in experimental NMR indicates specifically that the system being studied is not a PSS one (i.e., based on a dominant intracluster-coupling(s) in $\hat{\mathbf{L}}^{(0)}$) in the first case, but in reality is an isochronous spin system[20] which exhibits broken spin symmetry under evolution alone. A further all-too frequent oversight in the NMR literature concerns the (perceived) role of 3-space effects in PSS. These simply contribute the (maximal) specific rank and hence even/odd parity labelling[8,9,22] but of themselves can never induce PSS symmetry into the zeroth-order ensemble structure, $[\hat{\mathbf{H}}^{(0)},]_-$. The reader is referred to Abragam's classic text and illustrations[20], or the work of Jones et al.[7], for a fuller discussion of isochronous spin systems and (more importantly here) a further proof(s) concerning the non-symmetry breaking role of relaxation – as discussed in the former for the case of a $A[X]_2[^{35}Cl]_2$..-based spin system i.e., as subject to strongly dissipative quadrular relaxation. The contrasts in the lineshapes of the distinctive $[1^2]$, [2] salient spectral features of PSS is an established characteristic of such PSS problems, which is totally absent from the spectra of isochronous spin systems. Indeed, the observation of such $[1^n]$, $[n]$-based contrasts in the lineshape itself demonstrates the above point concerning the non-symmetry breaking roles of simple forms of $\hat{\mathbf{R}}_Q$, $\hat{\mathbf{R}}_{DD}$-induced relaxation i.e., governed by $[T^{2k''},.]_-$-based even outer-rank **R** terms.

APPENDIX

Multipole Expansions and Transformational Properties

The $\{T^{kq}(\nu)\}$ tensorial sets utilised in the main text are related to Sanctuary's $Y^{kq}(I)$ (as used in refs[9–11]) and thence to product basis density operator presentations, on noting that

$$T^{kq}(k_1 k_2) \sim$$

$$\sim 1/(\sqrt{(I_1)(I_2)}) \sum_{q_1, q_2} (-1)^{k_1 - k_2 + k} \sqrt{2k+1} (-1)^{k-q} \begin{pmatrix} k & k_1 & k_2 \\ -q & q_1 & q_2 \end{pmatrix} \mathcal{Y}^{k_1 q_1} \mathcal{Y}^{k_2 q_2} \qquad (A.1)$$

with the compaction $(x) = (2x + 1)$ being adopted here in the initial root expression. The $\mathcal{Y}^{k'q'}$ multipoles themselves (far RH side above) are related to product bases by a transformation. They are generated, within a Racah phase basis, from

$$\mathcal{Y}^{kq} = \mathrm{i}^k \sqrt{(I)(k)} \sum_{M, M'} (-1)^{I-M} \begin{pmatrix} I & k & I \\ -M & q & M' \end{pmatrix} |IM\rangle\langle IM'| \qquad (A.2)$$

where the bracket array simply represents 3*j* coefficient. The corresponding reverse transformation is also known, e.g., as given in Eq. (*28*) of ref.[10c].

The question of the inherent symmetry of $T^{kq}(11)$ tensors under dual symmetry is readily resolved by deriving their representations in terms of the simple Hilbert adapted $\{\alpha\alpha, (\alpha\beta + \beta\alpha)/\sqrt{2}, \beta\beta\}:\{(\alpha\beta - \beta\alpha)/\sqrt{2}\}$ forms, so that the dual tensors map directly onto $\{[\tilde{2}]:[\tilde{1}^2]\}$ subspatial salients of Liouville space. Hence one finds that

$$T^{11}(11) \equiv (1/\sqrt{2}) \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}; \quad T^{21}(11) \equiv (1/\sqrt{2}) \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \qquad (A.3)$$

$$T^{20}(11) \equiv (1/\sqrt{6}) \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 2 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}; \quad T^{22}(11) \equiv (1/\sqrt{2}) \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}. \qquad (A.4)$$

Hence both the $T^{11}(11)$, and the $T^{11}([\tilde{1}^2])$s associated with $J_{XX'}$ coupling, definitely lie in the antisymmetric salient whose forms are in distinct contrast to the various $[\tilde{2}]$, $T^{2q}(11)$ salient-based tensor components.

Some Comments on Analytic Spin Dynamics for the Contrasting Model B-PSS

Even without introducing a discussion of the consequence of applying limit conditions, it is clear as a question of logic that $\hat{\phi}^2_{\pm 2}(11)$ is actually uncoupled from all other polarizations, so that

$$\hat{\phi}^2_{\pm 2}(11)[t] = \exp(\pm i2wt)\,\phi^2_{\pm 2}(11)[0]\,. \qquad (A.5)$$

Hence on introducing the rotating frame, $\hat{\phi}^2_{\pm 2}$ represents a constant-of-motion, whose indirect observation clearly requires that one first generates some initial $\hat{\phi}^2_{\pm 2}[0]$ polarisation, as in the pulse sequences typical of 2D NMR experiments. For single quantum processes, the general AX spin system case[11] may be associated with distinctly labelled spin 1, spin 2 and a set of polarisations $\phi^1_q(10)$, $\phi^1_q(01)$, $\phi^1_q(11)$, $\phi^2_q(11)$ (where the last case is constrained to $q \leq 1$). The initial portion of Eq. (*1*) then yields for the rotating-frame case a typical coupled matrix equation, involving a set of initial conditions (as shown here on the right-hand side)

$$(\mathrm{d}/\mathrm{d}t)\begin{pmatrix} \hat{\phi}^1_1(10)[t] \\ \hat{\phi}^1_1(01)[t] \\ \hat{\phi}^1_1(11)[t] \\ \hat{\phi}^2_1(11)[t] \end{pmatrix} = \mathrm{i}\begin{pmatrix} \pm w_\mathrm{D} & 0 & -\mathrm{i}J/2 & 0 \\ 0 & \mp w_\mathrm{D} & \mathrm{i}J/2 & 0 \\ \mathrm{i}J/2 & -\mathrm{i}J/2 & 0 & w_\mathrm{D} \\ 0 & 0 & w_\mathrm{D} & 0 \end{pmatrix}\begin{pmatrix} \hat{\phi}^1_1(10)[0] \\ \hat{\phi}^1_1(01)[0] \\ \hat{\phi}^1_1(11)[0] \\ \hat{\phi}^2_1(11)[0] \end{pmatrix} \qquad (A.6)$$

based on $w_\mathrm{D} = (1/2)|w_{01} - w_{02}|$ as the off-set about the mean resonance, with the $\hat{}$ symbol of $\hat{\phi}^k_q(..)$s indicating the adoption of some form of rotating-frame. Formal solutions in this frame for the AX spin system have been discussed by Sanctuary[11]; the general solutions derived by standard methods are given as Eqs (*21*)–(*32*) and Table 5 of the 1985 Sanctuary work cited above. For brevity here, we just note that the derived $\lambda_{\pm i}$ eigenfrequencies are simply

$$\lambda_{\pm 1} = \mp J/2 \pm D/2\,; \text{ whereas } \lambda_{\pm 2} = \pm J/2 \pm D/2 \qquad (A.7)$$

where the quantity D has the form $\sqrt{(4w_D^2 + J^2)}$. These eigenfrequencies and their corresponding eigenvectors conveniently allow for the examination of limiting cases: i.e. of weak coupling, or of strong coupling between identical spins – as discussed below. On taking the expectation value for the sum of I_- operators as the specific NMR observable with a suitable initial condition, the spin dynamics for the weak coupled AX case furnishes the final solution

$$\langle\langle F_- \rangle\rangle[t] = (1 - \sin 2\theta)\cos\lambda_{\pm 2} t + (1 + \sin 2\theta)\cos\lambda_{\pm 1} t \qquad (A.8)$$

retaining like upper (lower) signs throughout, and where the specific initial condition used here was

$$\phi^1_{\pm 1}(10)[0] = \phi^1_{\pm 1}(01)[0] = \mathrm{i}/\sqrt{2}\ .$$

Finally, the observed spectrum is simply the Fourier transform of the spin dynamical Eq. (*A.8*). In consequence, the J interaction in this AX limit (corresponding to B-PSS) is an observable property, in direct contrast to spin dynamical result obtained for the XX′ spin case, involving dominant $J_{XX'}$ intracluster coupling between the identical spins.

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