On $SU(2) \times \mathcal{S}_{n \geqslant 12}$ dual-group tensorial sets and carrier spaces in the multiple invariant physics of multiquantum NMR. I. $k > n/2$ rank maximal $\{\sum_v T^k(v) \rightarrow \sum_{\widetilde{\lambda}'} \Lambda_{\cdot,\widetilde{\lambda}'}[\widetilde{\lambda}']\}$ Liouvillian $\widetilde{\mathbf{U}} \times \mathcal{P}$ mappings

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From the (automorphic) nature of nuclear permutational NMR spin symmetry established in the 1980s, the $SU(2) \times \mathcal{S}_n$ tensorial sets exhibit simple reducibility (SR) over their pattern algebraic-based Liouvillian carrier space [F.P. Temme, Physica A 166 (1990) 676; 198 (1993) 245; Chem. Phys. 238 (1998) 245] for NMR. This underlies the quantum physical role of the $\mathcal{S}_n$ group and its fundamental set of system invariants (SIs), i.e. beyond the Cartesian SIs of [P.L. Corio, J. Magn. Reson. 134 (1998) 131]. Here we examine the *outer*-rank dual-group tensorial subsets (over a $\{[\widetilde{\lambda}]\}(\mathcal{S}_n)$ field) as standardised maximal forms for all $\lambda \vdash n$: $(\lambda < (n/2))$ weakly-branched partitions. Techniques based on Schur functions (SFs) "on a restricted subspace (RSS)", classics in the Wybourne–Butler atomic physics tradition, serve to highlight the central role of combinatorics in physics. Recursive use of the SFs/RSS from the skew-diagonals of $\{|I\overline{M}\rangle, \ldots, |I\overline{M}\rangle\}$ square generates the rank-alone structure of Liouville space from SR $\mathcal{S}_n$ decompositions of individual *bipartite* SF products. For high enough n-indexed groups, the tensorial subsets exhibit *maximal standard* forms. Within a total $\binom{2n}{n}$-fold space, the $\{T^k(k_1, k_2, \ldots, k_n : \mathcal{S}_n)\}$ $(k = k_{\max} - i)$th subdimensionalities are governed by the related $\chi^{[2n-i,i]}_{1^{2n}}(\mathcal{S}_{2n})$ characters. The use of three separate combinatorial algorithms yields the

$$\Big\{ \sum_v T^k(v) \rightarrow \big\{ \big[\widetilde{\lambda}\big] \big\} \,\big|\, p \leqslant 2^2 \text{ part} \Big\}$$

maps as the origins of subsequent studies (of part II) on democratic invariants. A strong case for the retention of $\mathcal{S}_n$ group in NMR has been made in our above-cited papers, in the context of spin dynamics [B.C. Sanctuary and T.K. Halstead, Adv. Opt. Magn. Reson. 15 (1991) 197; and references therein], and by [J.J. Sullivan and T.H. Sidall-III, J. Phys. Chem. 96 (1992) 5789] for state-space. The present work relates specifically to NMR evolution and to coherence transfer processes. Our understanding of spectral nuclear spin statistical weights of uniform fermionic (bosonic) cage-isotopomers (as, e.g., in the ro-vibrational CNP of $^{13}C_n$ fullerenes) benefits from an appreciation of the dual group and its carrier space.

1. Introduction

The structure of dual-group tensorial sets, beyond the original covariance properties given in Racah and Fano [22], or in the work by Coope on the $(\otimes SU(2))^n$ formalism [18] from 1970 (see also [1–7] cited in [18]), play a pivotal role in incorporating *democratic* methods [23,37] (rather than graph-theoretic approaches [41,33]) into physics. The former are based on certain underlying scalar invariants and of pertinence to molecular ensemble-based quantum Liouville (QL) descriptions of NMR spin dynamics [45], where the latter may include the physics of both evolution and intracluster relaxation. Since the following discussion focuses on *transformational* properties associated with *system invariants under the dual group*, it also has pertinence (for reasons stated below) for the Hilbert-space-based fermion (or boson) nuclear spin statistical weighting properties [7] of highly symmetrical (here in the 3-space sense) single-isotopomeric cage structures, a topic of much recent chemical interest.

In developing these conceptual ideas here, it is convenient to stress Liouville space models under group actions, which underlie such transformational properties, for their explicit involvement of the dual group auxiliary invariant labels of the quantum physics associated with carrier spaces. In contrast to [18], or to the (Hilbert space) work of Lévy-Leblond and Lévy-Nahas [37], which both essentially focus on few-body spin recoupling formalisms – and their relationship to established (Sanctuary–)Jucys [33,41] graph theory (JGT) (of 1970s) – more recent work [51,53–55,60,62] has sought to encompass *truly n-body* spin interactions [9,10] governed by an extensive set of purely $(SU(2)\times)\mathcal{S}_n$ scalar invariants (SIs), as in papers [55,60]. This necessarily draws on certain essential aspects of quantum physics [9,10,17,42,48,49], which introduce the roles of carrier spaces [9,10,53–55,60,62], as well as symmetry properties under $\mathcal{GL}_n \supset \cdots \supset \mathcal{S}_n$. We stress that the structures of the former are rather more than simply classifications, on account of their inseparability from the essential invariant and transformational physical properties. This is particularly the case for nuclear spin ensemble problems. Naturally, in handling the scalar invariants of these spin ensembles one only needs to consider the $SU(2) \times \mathcal{S}_n$ algebras and their group actions [54,55,60,62].

The wider $SU(m) \times \mathcal{S}_n$ forms for the dual group constitute the most general spectroscopic form; beyond the question of the nature of system SIs addressed here and in [62], these forms apply to higher-I nuclear spin (NS) problems over $\{k, q, v\}$ labels [33,41,45], once one is concerned with details of specific dynamical NMR processes [42,45], from some known initial condition. Likewise, such dual symmetries determine the (Hilbert-space-based) spectral NS statistical weights, via so-called complete nuclear permutation (CNP) effects [7] inherent in isotopomeric (cage) ro-vibrational spectra. Naturally, the use of dual group symmetry [9,10,53–55,60,62], which itself draws on various aspects of group structure [12,13,17,29,34–36,40,48,49,59,63,68,70] and of tensorial QL formalisms [33, 38,41–43,45,46], is less restricted than, e.g., the commonly utilised (but restricted) product, or $|I\overline{M}(\ldots)\rangle\langle I\overline{M}(\ldots)|$ "projective" descriptions of NMR (NQR) processes. This is so on account the former being a general spectroscopic approach based on $\{T^{kq}_{\{\ldots\}}(\bar{v} = k_1, \ldots, k_n)\}$ recoupled bases, within which the $\{k, q\}$s, or outer rank and z-projection entities, correspond directly to $I, \overline{M}$ of the $\{|I\overline{M}(i_1, \ldots, i_n)\rangle\}$ Hilbert basis. The distinctions [45] between tensorial and shift operator bases are important.

The NMR dual-group tensorial techniques invoked in our 1990–1998 work [53, 55,60] rest on unitary (and $\mathcal{S}_n$-Yamanouchi symbol-based [9]) projective boson mapping over (dual group) Liouvillian carrier space, as a product-space-based extention to Biedenharn and Louck's Hilbert space boson-algebraic formalisms [9,10] of the early 1980s. The study of NMR evolution [3,14,19–21,24,30–32,38,43,45,46] (or of intracluster relaxation, or coherence transfer [38]) for multiquantum, multispin systems extends Sanctuary's early theoretical work on QL-NMR (as covered in [33,41,42,45]), which had utilised JGT recoupling methods in the context of density matrix formalisms, e.g.,

$$\sigma \equiv \sum_{k=0}^{k_{\max}} \sum_{q=-k}^{k} T^{kq}(v)\phi^k_q(v). \tag{1}$$

This is formulated here in terms of outer k, q multispin tensorial bases [38,42,43,45,46] via standard graphical recoupling methods [33,41], in which the auxiliary v contains $\bar{v}, \{\widetilde{\mathcal{K}}\}$, which are obtained respectively from the local k_is (constituting an inner field) and the recoupling labels. Hence, one arrives at the following simple unitary-group-based tensorial expressions, where the $(i)^k$ phase and $(2I+1)^{-1/2}$, $(2k+1)^{-1/2}$ normalising terms have been omitted for brevity:

$$\mathcal{Y}^{kq} \sim \sum_{MM'} (-1)^{k-q} \begin{pmatrix} I & k & I \\ -M & q & M' \end{pmatrix} |IM\rangle\langle IM'|, \tag{2}$$

for generalised projection formalisms based on single spin, and

$$T^{kq}(v) \equiv |kqv\rangle\rangle \sim \sum_{q'q''} (-1)^{k-q} \begin{pmatrix} k & k' & k'' \\ -q & q' & q'' \end{pmatrix} \mathcal{Y}^{k'q'}\mathcal{Y}^{k''q''} \tag{3}$$

(or more generally, $T^{kq}_{\widetilde{\mathcal{K}}}(\bar{v} = (1_1, \ldots, 1_n))$, now over some more generalised recoupling graph-scheme for multispin-based tensors). Hence, it follows that the *physical NMR observables* are simply the $\phi^k_q(v)$ coherences (polarisations) obtained on evaluating certain trace relationships, as, e.g., in

$$\phi^k_q(v) = \langle\langle T^{kq}(v) \,|\, \sigma\rangle\rangle \equiv \mathrm{tr}\{(T^{kq}(v))^\dagger \sigma\}, \tag{4}$$

which we shall return to later. It suffices in passing to note that conventional NMR involves detecting the ϕ^1_1 coherences, whereas other spin resonance techniques, such as, e.g., nuclear acoustic resonance (NAR), detect the ϕ^2_2, ϕ^2_1 coherences.

In the context of Balasubramanian's approach to NMR spin symmetry [3] via automorphisms (based on the equivalences inherent in the spin–spin interactions constituting a network), papers [53,55,60] give a fuller understanding of the physical significance of the idea of simple reducibility (SR), as it applies to the carrier space(s) associated with $SU(2) \times \mathcal{S}_n$ tensors and their auxiliary labels. Dual group projective actions as $\widetilde{\mathbf{U}} \times \mathcal{P}(\mathcal{S}_n)$ mappings derive from boson-pattern formalisms [9,54,55,60,62] of $\{|IM(i_1, \ldots, i_n)\rangle\}$ Hilbert space [10]. These ideas were extended in [55] to Liouville space in order to establish the *completeness* of the following set, *both* as dual group representations and as a *definition of all possible transformations* inherent in the physical modelling. In the context of the completeness of projective mappings for Liouville formalisms of spin dynamical NMR problems (see below), these sets over the auxiliary v terms yield the following dual irreps:

$$\left\{D^k(\widetilde{\mathbf{U}}) \times \widetilde{\Gamma}^{[\lambda]}(v)(\mathcal{P}) \,\middle|\, \widetilde{\mathbf{U}} \in SU(2); \widetilde{\Gamma}^{[\lambda]}(v),\ \mathcal{P} \in \mathcal{S}_n\right\}. \tag{5}$$

This comes about as a result of invoking the appropriate $\widetilde{\mathbf{U}}$ unitary group action and the corresponding $\mathcal{P}(\mathcal{S}_n)$ action (as realised via the use of Yamanouchi symbols [9]) over the $\widetilde{\mathbb{H}}$ carrier space. Here from comparisons with [9,10], one notes that the additional auxiliary v parameters of $\widetilde{\Gamma}^{[\lambda]}(v)$ are now *explicit parameters* of these Liouvillian $\widetilde{\mathbf{U}} \times \mathcal{P}$ actions, and so inherent in the dual group projective mappings over the carrier space $\widetilde{\mathbb{H}}$. Their role is to include *all* the underlying scalar invariants of the multispin system in a systematic totally *democratic* (i.e. non-JGT) manner. Hence, from the distinct auxiliary terms, now with both $\bar{v}$ (as above) and – on replacing the $\widetilde{\mathcal{K}}$ simple unitary recoupling terms (of [55]) by $\widetilde{\mathcal{V}}$ – the corresponding democratic recoupling components, the overall carrier space is found to span a set of (democratic labelled) subspaces:

$$\widetilde{\mathbb{H}} \equiv \sum_v \widetilde{\mathbb{H}}_v. \tag{6}$$

Naturally, this contains the required necessary and sufficient conditions for the retention of SR in Liouville space, based on specific component democratic scalar invariants of recent general expositions [55,60]. Some discussion of applications of carrier spaces in quantum physics may be found in these papers. Since these auxiliary terms arise from structures based on $\mathcal{S}_n$ induced democracy, they may be treated as arising from the known (1987) properties of Yamanouchi $\mathcal{S}_n$ group chains (YGC) [17,48,49]. The presentation in the subsequent work [62] develops ideas concerning specific indexed $\mathcal{S}_{(n=12)}$ YGC-hierarchies – i.e. as specifically derived from the present (superboson) mappings onto the $\{[\widetilde{\lambda}] \mid p \leqslant 4\}$ set.

In order to give actual examples of the nature of these democratic invariants (cf. orthogonal forms of [20]), one first needs to cast the problem into a symbolic algebraic combinatorial form [35], and then utilise the properties of Schur functions (SFs) [12,13,68]. For generality, it is convenient to examine the rank-alone tensorial structure (cf. [51]) and to focus on the $k > (n/2)$ rank subspaces, i.e. of a sufficiently high n-indexed dual group to ensure that weak partitional branching will yield certain forms of *maximal* mappings [59,63]. The present paper, with its focus on the generality of the $\mathcal{S}_{12}$ [70] or $\mathcal{S}_{n>12}$ algebras, utilises several of the general symbolic algorithms of [35,40] and various standard theorems applicable to permutation groups [29,34,36], in setting up the formalism for $SU(2)\times\mathcal{S}_n$ mappings from a square on the full (outer) $\{|I\overline{M}(i_1,\ldots,i_n)\rangle\}$ Hilbert space. Specific rank tensorial components arise from a sum of products over some (minor) skew-diagonal. Certain bipartite SF products (SFPs) and more general simple SF decompositions applied to the resultant structure then yield the dual tensorial forms and their mappings onto Liouville space. Irrep sets of the latter are denoted here with a tilde accent over the partition λ, as in $\{[\widetilde{\lambda}]\}$. The specifics of the different component SFP, or SF decompositions are given in section 2 below. The following paper [62] sets out concise descriptions via a reduction coefficent hierarchy for the various distinct scalar invariants, or v auxiliary labels, specific to $\mathcal{S}_{12}$ dual tensors, by utilising the general YGC concepts of our 1998 work [60]. A description of the physical context to studies of NMR evolution (or intracluster relaxation) involving permutation (over $(k_1,\ldots,k_n)$) is given, for which dual tensorial bases [38,43,46] are appropriate for strong intracluster (and conventionally weak intercluster) interactions [3,14,19–21,24,30–32,38].

One arrives at a matrix-differential equation formalism [42,43,45,46], the quantum Liouville equation (QLE), for $-\mathrm{i}d_{(t)}\phi_q^k(v:[\widetilde{\lambda}])$, determined (over the $[\widetilde{\lambda}](\mathcal{S}_n)$ subspaces) by

$$\sum_{k''q''v''}\big\langle\big\langle kqv:[\widetilde{\lambda}]\big|\widehat{\mathcal{L}}^{k'q'}\big(v':[\widetilde{n}]\big)\big|k''q''v'':[\widetilde{\lambda}]\big\rangle\big\rangle\phi_{q''}^{k''}\big(v'':[\widetilde{\lambda}]\big)(t=0), \tag{7}$$

where the experimental observables, the factored $\phi_q^k(v:[\widetilde{\lambda}])$ coherences, are obtained directly from the density matrix, with the use of some suitable initial condition [38]. The Liouvillians retain the automorphic permutational spin symmetry being "$[\widetilde{\lambda}=\widetilde{n}]$ totally symmetric to zeroth order"

$$\widehat{\mathcal{L}}\equiv\big[\widehat{H}^{\text{intr}}_{\text{SC}}\big([\widetilde{n}]\big)^{(0)}+\widehat{H}^{\text{intercl}}_{1:\text{SC}},\cdot\big]_{-}, \tag{8}$$

by virtue of one or other of the appropriate general forms [3,14,19–21,24,30–32] involving weak $\{J_{AX},\ldots\}$-based $[\widehat{H}^{\text{intercl.}}_{1:\text{SC}},\cdot]_{-}$ (or similar isotropic dipolar) intercluster terms. Alternatively for isotropic dipolar case, the Liouvillian becomes

$$\widehat{\mathcal{L}}_{\text{SC+IDD}}\equiv\big[\widehat{H}^{\text{intr}}_{\text{SC+IDD}}\big([\widetilde{n}]\big)^{(0)}+\widehat{H}^{\text{intercl}}_{1:\text{SC+IDD}},\cdot\big]_{-}, \tag{9}$$

within which the intra-/intercluster relationships $\{J_{AA'},\ldots\},\{J_{XX'}\}\gg\{J_{AX},\ldots\}$ apply, or in the liquid crystalline media dipolar NMR case, involves a similar ordering of the corresponding $\overline{D}_{AA'},\ldots,\overline{D}_{XX'},\ldots,$ isotropic dipolar interactions [14,20]. In passing, it is worthwhile recalling that it is the equivalence within the various regular networks of $J_{AA'}$, $J_{XX'}$ interactions which leads to the group automorphisms originally introduced into NMR by Balasubramanian [3]. Since all the invariants and time-reversal symmetries are already incorporated into the above dual group tensorial modelling of equation (7), it must represent all the transformational properties and accessible physics inherent in this type of NMR spin problem. With the outer spin (super)operators $\mathcal{F}^2$, $\mathcal{F}_z$ in explicit forms, as implied by $\widehat{F} = \sum_i^n \widehat{I}_i$, the question of their $[\widehat{F}\bullet, [\widehat{F}, \cdot]_-]_-$, or $[F_z, \cdot]_- \equiv [\sum I_{zi}, \cdot]_-$ actions and of the role of the scalar $(k_1, \ldots, k_n)$ field term in defining good quantum numbers may be presented as in equations (2)–(4) of [42]; paper [55] discusses these points also, in the context of superbosons as superoperators. Since the form of these expressions and of the Liouvillian $\mathcal{F}_\pm$ ladder operators has been reported in earlier work [55,60], they are not given here, for brevity.

A physical understanding of coherence transfer process was initially obtained by Sanctuary [45] using analytic methods based on Laplace-transform techniques. Beyond this AX system, the appropriate form of QLE incorporating symmetrised bases provides insight into the *penultimate maximal multiquantum* coherence transfer processes $\phi_{q=k}^{k=n-1}(1_1, \ldots, 1_n : [\widetilde{n-1, 1}])$ of the $[A]_2$ and $[A]_3$ spin systems [38,43,46]. Similarly the multiquantum multispin coherences of higher ensemble $\mathcal{S}_4 \downarrow \mathcal{D}_2$ spin systems have been examined, e.g., in a 1998 liquid-crystal solvent media high-resolution NMR studies [14]. Here the appropriate Liouvillian contains both intracluster (ring, or molecular) $\overline{D}_{AA'}$, $\overline{D}_{XX'}, \ldots$ isotropic dipolar and $J_{AA'}$, $J_{XX'}, \ldots$ scalar couplings. In a recent NMR symmetry treatment of invariants [20], Corio has extended various earlier (orthogonal-group-based) views of NMR spin symmetry over $\{|I\overline{M}(i_1, \ldots, i_n) : [\lambda]\rangle\}$ space [19,21,24,30–32]. However, no mention was made in [20] of either the *automorphic* nature of spin symmetry [3], or indeed of the $\mathcal{S}_n$ group – the latter is a curious omission, since all the common spectroscopic finite groups are subgroups of the symmetric group *by virtue of Cayley's theorem* [17], indicated in subduction hierarchy of equation (14a) below. Inclusion of the $\mathcal{S}_n$ group in NMR spin symmetry is a *direct consequence* of the use of nuclear spin permuational automorphisms [19,21,24,30–32] in the 1980s, ideas which apply equally to CNP statistical-weight-based properties. Indeed, this is the essential property that allows (Liouvillian) NMR to be treated via the *dual group* quantum physics of *quasi*particles [9,10] and its associated *mapping* techniques [53,55,60] over Liouville space.

Specific details of the nature of $[A] \equiv [^{13}\mathrm{C}]_n$ and certain $[AX]_n$ (bi-)cluster statistical weights have been given in the work of Balasubramanian [4,5,7,8] and others [26,56–58,61,66]. Indeed, one of the earliest [8] of these ro-vibrational spectral studies [4,5,8,58,61] mentions the spin statistical weights of the simple $[\mathrm{H}]_{12}$ spin cluster, over $SU(2) \times \mathcal{S}_{12}$, as a component of the full 12-fold borohydride anion. However, this work did not refer explicitly to the underlying $\chi^{[\lambda]}(\mathcal{S}_{12})$ group characters [70]. Since neither $\mathcal{S}_{12} \downarrow \mathcal{I}$, nor $\mathcal{S}_{20} \downarrow \mathcal{I}$ constitute Cayley criteria embeddings, the state-space enumerations of the corresponding $[^{11}\mathrm{B}]_{12}$ and $[^{10}\mathrm{B}]_{12}$ ($SU(m)$) monoclusters are of some specific interest [58,61] in the context of their mathematical determinacy for the group embeddings associated with cage isotopomers. Universal mathematical determinacy of $\mathcal{S}_{12} \downarrow \mathcal{I}$ natural embeddings was established [61] from the *completeness of the unique* $1:1$ *bijective subductional mapping*. The pertinence of this result to ro-vibrational spectroscopy is a consequence of the total spin/orbital symmetry being physically constrainted [4,7] by the following criteria:

$$\Gamma^{\text{spin}}(\text{CNP}) \times \Gamma^{\text{orbit}}\big(O(3) \downarrow \mathcal{G}\big) \sim \begin{cases} \mathcal{A}_2, \\ \mathcal{A}_1, \end{cases} \tag{10}$$

for uniform fermion (boson) particles, respectively. For other examples of the spectroscopic impact of CNP statistics, the reader is referred to a couple of review articles [4,56] and certain CNP-based works [26,57,66], which retain the $\mathcal{S}_n$ group in their discussion of $\mathcal{S}_n \downarrow \mathcal{G}$ natural embedding processes, in preference to utilising $\mathcal{O}(3) \downarrow \mathcal{G}$ notation; of course, vibrational spectroscopy [1,26,27] is the natural domain of the orthogonal group chain.

There is no direct analogy between CNP cage/ring isotopomers properties and deceptive NMR of ring-molecules, which occurs in ensemble NMR when one or other of the inter-cluster spin interactions are of a significant magnitude, compared to the intracluster sets of couplings. The CNP spin statistics is taken over equivalent set(s) of quasi-polyhedral vertex points associated with each distinct set of uniform fermions/bosons.

The present work is structured as follows. Section 2 sets out the basis of the symbolic algebraic modelling, for tensorial sets based on Schur functions (SFs) and particularly on SF products (SFPs). This treats individual SFP on "restricted spaces" within the context of the role of $\mathcal{GL}_n$ subgroups. Equations (12)–(15) set out the individual SFP decompositions on $\mathcal{S}_n$ SF space. Section 3 utilises these results in context of certain (minor) skew-diagonal sums of figure 1 to evaluate all the $k > (n/2)$ (maximal) mappings, which are then shown (in section 4) to be amenable to factorisation into subsets, corresponding to the invariant-based $\widetilde{\mathbb{H}}_v$ carrier subspaces. Section 5 briefly discusses our conceptual results as they relate to both fundamental theory and to use of the symmetric group in modern NMR and CNP studies. However, the distinct $\mathcal{S}_n$-democratic invariants themselves, via a somewhat lengthy hierarchical process over $\mathcal{S}_{n-1} \supset \cdots \supset \mathcal{S}_{n-i} \supset \cdots \supset \mathcal{S}_2$ subgroups, and their quantum physics are the subject of a subsequent paper [62]. Various ancillary points of detail in the symbolic modelling process for the $\{[\widetilde{\lambda}]\}$s spanned by the kth-rank carrier subspaces may be found in tables 1, 2 or in the appendix. Section 6 summarises certain fundamental aspects of the work, particularly in the context of recent interest in the roles of automorphic (group) and more general networks in science.

The notation utilised throughout derives directly from those either of Wybourne [68], or of Biedenharn and Louck – as subsequently extended to Liouville space in [55] – or else corresponds to the NMR spin dynamics notation utilised by Sanctuary and Halstead [45]; with exception of pulse sequence "COSY" [2], NMR jargon has largely been avoided in this article. In particular, we would stress that the standard terminology of group theory and algorithmic algebraic combinatorics pertaining to the symmetric group, SFs and Yamanouchi chains is well-established and may be found in the mathematical texts of Sagan [40], James and Kerber [29], or Kerber [34] or else in Biedenharn and Louck [9,10]. Chen's 1987 symmetry text [17], or the more recent monograph due to Sternberg [48], as well as Wybourne's [68] standard mathematical physics, all discuss various physical applications of symmetry properties, similar to those utilised herein.

2. Symbolic combinatorial modelling underlying dual tensorial sets

On recognising the specialised nature of *bipartite* $\lambda \vdash n$ Schur functions (SFs), i.e. as representations of $\mathcal{GL}_n$ groups, one introduces (utilising Butler's notation [12], which simply suppresses the leading $n-\mu$ terms, as redundant for known n-index) SFs via

$$\{\hat{\mu}\} \equiv \{\widehat{n-\mu,\mu}\} \quad \text{and} \quad [\mu] \equiv [n-\mu,\mu], \quad \text{where } \{\hat{0}\} \equiv [0]; \tag{11}$$

this initialises (specifically below for "even" n-indices) the specialised hierarchy of irreps derived from bipartite SFs for $i = \mu$ integer, as in

$$\{\hat{\mu}\} \equiv [0] + [1] + \cdots + [i], \quad \forall i < (n/2) \quad \text{to} \tag{12}$$

$$\{\widehat{(n/2)}\} \equiv \sum_{i=0}^{(n/2)} 1[i], \tag{13}$$

the final bipartite-SF form. Such hierarchies for bipartite SFs constitute *simply-reducible* (SR) decompositions [29,34,36,40] under Young's rule (YR-III) (onto the $\{[\lambda]\}$ set). For the more general multipartite SFs, YR-III enumeration (in a non-SR form) is a well-established part of (symbolic) algorithmic combinatorics [29,34–36,40]. From Butler and King's discussions [12,13] of (alternative) subgroup subduction chains of the $\mathcal{GL}_n$ group and its (ordered) subgroups, one obtains the details of the (interlinked) group chains as

$$(\mathcal{G})\mathcal{L}_n \supset \mathcal{O}_n \supset \mathcal{O}_{n-1} \supset \mathcal{S}_n \supset \mathcal{G}, \tag{14a}$$

$$\cdots \supset (\mathcal{G})\mathcal{L}_{n-1} \supset \mathcal{O}_{n-1} \supset \mathcal{S}_n \supset \mathcal{G}. \tag{14b}$$

The idea of the n-indexed symmetric group being a subgroup of the $\mathcal{GL}_n$ group is central to the use of mappings onto restricted subspaces [68], as invoked here. Specifically for exclusively bipartite SFP, the latter may be shown to take on further interesting SR forms in the restricted subspace, see equations (19)–(22) below. This seems to have been overlooked in the discrete mathematics literature, as restricted subspace techniques were developed essentially by the atomic spectroscopy and theoretical physics community.

In the present work, we are concerned with the additional consequence of utilising certain restricted subspaces (RSS) for specific subgroups within some ordered hierarchy derived from the general linear group. The subgroups of $(\mathcal{G})\mathcal{L}_n$ considered here lie *beyond* those covered, either in Wybourne's 1970 treatise [68] on atomic physics applications, or else in [12,13]. For *bipartite* SF-products, one may recognise simpler intermediate structures; these are in addition to the generalised Weyl–Schur isometries for SFs on $\mathcal{GL}_n$, *contrasted* to the corresponding irreps on $\mathcal{S}_n$ space [48]. A specific form of this well-known isometry yields identical reduction coefficients over the sets (fields) for SFs ($\mathcal{GL}_n$) and symmetric-group *inner products* (IPs), for SFs (irreps) respectively, as in

$$\{\hat{\mu}\} \otimes \{\hat{\mu}''\} \to \sum_{\mu'} \Lambda_{\otimes,\mu'} \{\hat{\mu}'\}, \tag{15}$$

$$[\mu] \otimes [\mu''] \to \sum_{\mu'} \Lambda_{\otimes,\mu'} [\mu']. \tag{16}$$

Apart from its application to IPs, other isometries (e.g., those involving outer products) occur [48], as discussed in the appendix. On re-interpreting one aspect of equations (14) and (15) above (here again *specifically for bipartite* SFs and for sufficiently high n-indexed groups), with $\xi_{\varrho\varphi}$ (pairwise) signed integers for some particular SF product on the RSS, it follows that

$$\begin{aligned} [\mu] \otimes [\mu''] &\to \left(\{\hat{\mu}\} - \{\widehat{(\mu-1)}\}\right) \otimes \left(\{\hat{\mu}''\} - \{\widehat{(\mu''-1)}\}\right), \quad \text{or} && \text{(17a)} \\ &\to \sum_{\text{all poss. } \varrho\varphi \text{ pairs}} \left((\xi_{\varrho\varphi})\{\hat{\varrho}\} \otimes \{\hat{\varphi}\}\right)(\mathcal{S}_n) \\ &\to \sum_{\varrho\varphi \text{ pair decomp.}} (\xi_{\varrho\varphi}) \left\{ \sum_{\mu'''} 1\{\hat{\mu}'''\}(\mathcal{S}_n) \right\}, \quad \text{so} && \text{(17b)} \end{aligned}$$

$$[\mu] \otimes [\mu''] \to \cdots \to \left(\sum_{\mu'} \Lambda_{\cdot,\mu'} [\mu'] \right), \tag{18}$$

where the original bipartite SFP SR properties are now overridden by the subsequent $\xi_{\varrho\varphi}$ (*signed*) small integers of the outer sum (over all $\varrho\varphi$ pairs), to yield the final (non-SR) sets of composite reduction coefficients $\{\Lambda_{\cdot,\mu'}\}$.

This two stage process is valuable, both from the viewpoint of its physics versus mathematics correlation, as set out in equation (26) below, and because the individual SF products now may be enumerated on the restricted S_n subgroup space. The latter is simply reducible and the right-hand components of equations (19)–(22) constitute subsets of the corresponding $\mathcal{GL}_n$ sets of (inner) SFPs. Clearly, the preliminary form, i.e. equation (17a) and the inner-most sum of the final step (17b) (now over $p \leqslant 2^2$ part forms) are based on simple Young-rule (III) decompositions [34–36,40].

For the second stage above (i.e. equation (17b)) within the dimensionality constraints to the *bipartite* inner products, the specific mappings, i.e. as minimal SR subsets of the overall $\mathcal{GL}_n$ IP isometry properties, arise from the following $\mathcal{S}_n$ *restricted subspace* decompositions:

$$\begin{pmatrix} \{\hat{1}\} \otimes \{\hat{1}\} \\ \{\hat{2}\} \otimes \{\hat{2}\} \\ \{\hat{3}\} \otimes \{\hat{3}\} \end{pmatrix} \to \begin{pmatrix} \{\hat{1}\} + \{\widehat{11}\} \\ \{\hat{2}\} + \{\widehat{111}\} + \{\widehat{22}\} \\ \{\hat{3}\} + \{\widehat{211}\} + \{\widehat{221}\} + \{\widehat{33}\} \end{pmatrix} (\mathrm{RSS}:\mathcal{S}_n), \tag{19}$$

$$\begin{pmatrix} \{\hat{1}\} \otimes \{\hat{2}\} \\ \{\hat{1}\} \otimes \{\hat{3}\} \\ \{\hat{1}\} \otimes \{\hat{4}\} \\ \{\hat{1}\} \otimes \{\hat{5}\} \end{pmatrix} \to \begin{pmatrix} \{\widehat{11}\} + \{\widehat{21}\} \\ \{\widehat{21}\} + \{\widehat{31}\} \\ \{\widehat{31}\} + \{\widehat{41}\} \\ \{\widehat{41}\} + \{\widehat{51}\} \end{pmatrix} \ (\mathrm{RSS}:\mathcal{S}_n), \tag{20}$$

$$\begin{pmatrix} \{\hat{2}\} \otimes \{\hat{3}\} \\ \{\hat{2}\} \otimes \{\hat{4}\} \\ \{\hat{2}\} \otimes \{\hat{5}\} \end{pmatrix} \to \begin{pmatrix} \{\widehat{21}\} + \{\widehat{211}\} + \{\widehat{32}\} \\ \{\widehat{22}\} + \{\widehat{311}\} + \{\widehat{42}\} \\ \{\widehat{32}\} + \{\widehat{411}\} + \{\widehat{52}\} \end{pmatrix} \ (\mathrm{RSS}:\mathcal{S}_n), \tag{21}$$

$$\begin{pmatrix} \{\hat{3}\} \otimes \{\hat{4}\} \\ \dots \end{pmatrix} \to \begin{pmatrix} \{\widehat{31}\} + \{\widehat{221}\} + \{\widehat{321}\} + \{\widehat{43}\} \\ \dots \end{pmatrix} \ (\mathrm{RSS}:\mathcal{S}_n). \tag{22}$$

Here we note that the actual number of terms in the RSS-decomposed specialised bipartite-SF inner products is precisely one more than the numerical argument of the lower SF. Additional properties of bipartite SF inner products on RSS are discussed in more detail elsewhere [63], utilising still higher n-indexed symmetric groups, so as to include a wider range of maximal mappings.

As a final preliminary statement, we would stress the structured nature of "$\rhd$ *dominance ordering*" [40] for SFs (omitting here the SF braces { } within the set, for brevity) and $[\mu]$ irreps in the following pair of comparable forms:

$$\begin{aligned} \widehat{\mathcal{L}}^{\dagger}_{\mathrm{RS}}(\mathrm{SF}/\mathcal{S}_n) \equiv \{&\hat{0}\ \hat{1}\ \hat{2}\ \widehat{11};\ \hat{3}\ \widehat{21}\ \widehat{111};\ \hat{4}\ \widehat{31}\ \widehat{22}\ \widehat{211}\ 1^4;\ \hat{5}\ \widehat{41}\ \widehat{32}\ \widehat{311}\ \widehat{221}\dots; \\ &\hat{6}\ \widehat{51}\ \widehat{42}\ \widehat{411}\ \widehat{33}\ \widehat{321}\}, \end{aligned} \tag{23a}$$

$$\begin{aligned} \mathcal{L}^{\dagger}(\mathcal{S}_n:\rhd\,\mathrm{ord.}) \equiv \{&[\tilde{0}]\ [\tilde{1}]\ [\tilde{2}]\ [\widetilde{11}];\ [\tilde{3}]\ [\widetilde{21}]\ [\widetilde{111}];\ [\tilde{4}]\ [\widetilde{31}]\ [\widetilde{22}]\ [\widetilde{211}];\ [\tilde{5}]\dots; \\ &[\tilde{6}]\dots[\widetilde{33}]\ [\widetilde{321}]\}, \end{aligned} \tag{23b}$$

introduced here on account of their use as right-hand column vectors in the text.

3. Tensor rank-alone set formation on $\{|IM\rangle, \dots, |I0\rangle\rangle, \dots, |I-M\rangle\rangle\}$ space

One writes for compactness:

$$\sum_{v} T^{k'}(v) = \left\{ \sum_{v} T^{k_{\max}-i}(v:\mathcal{S}_n) \,\middle|\, 0 \leqslant i \leqslant (n/2); k' \leqslant k_{\max} \right\}, \tag{24}$$

	$\mathcal{Z}_i$: LS $\rightarrow$	$\{0\}$	$2\{1\}$	$2\{2\} + \{1\}^{\otimes}$	$2(\{3\} + \otimes^{1,2})$
$- - --$					
$\{\hat{\mu}\} :\rightarrow$					
$\downarrow$					
$\{0\}$	$\{0\}$	$\{1\}$	$\{2\}$	$\{3\}$	$\{4\}$ ...
$\{1\}$	$\{1\}$	$\{1\} \otimes \{1\}$	$\{1\} \otimes \{2\}$	$\{1\} \otimes \{3\}$	
$\{2\}$	$\{2\}$	$\{1\} \otimes \{2\}$	$\{2\} \otimes \{2\}$		
$\{3\}$	$\{3\}$	$\{1\} \otimes \{3\}$			
$\{4\}$	$\{4\}$				
..	..				

Figure 1. The skew-diagonal sums ($\mathcal{Z}_i$) generating Liouvillian rank-alone tensorial subsets, as described in section 3 of the text.

and recalls that the correspondence between Hilbert space spin states and the initial forms of $\mathcal{S}_n$ irreps (SFs) takes the form

$$\big|I\big(M \equiv (n/2) - i\big)\big\rangle \equiv \sum_i [i] \equiv \big\{\hat{i}\big\}, \quad \forall i < n/2, \tag{25}$$

to the maximal bipartite form.

On recalling the structure of the (schematic) Liouville space "generator" of figure 1, itself based on the nature of SF-IP decompositions on restricted space SFs, the resultant (initial (minor)) *skew-diagonal* sums ($\mathcal{Z}_i$) of SF-IPs provide the Liouville space structure. Since we are considering (in contrast to the original $\{|kqv\rangle\rangle\}$ forms of an earlier preliminary work [51]) the *rank-alone* tensorial sets on $\{k, v\}$ subspaces, it is necessary to invoke a recursive adjacent skew-diagonal-sum (or $\mathcal{Z}_i$) *difference formalism,* or

$$\text{for } k' = k_{\max} - i\text{:} \quad \sum_v T^{k'}(v) \equiv \mathcal{Z}_i - \mathcal{Z}_{i-1}, \tag{26}$$

where these (minor) skew-diagonal sums are (in terms of geographic orientations) from the SW-to-NE triangular subsets of these SFP terms.

Hence, one obtains the tensorial subset-to-restricted space SF mapping relationship, given here with (on LHS) the decreasing rank specific subdimensionalities, respectively of the $n = 12,\ 20$ $\mathcal{S}_n$ group tensorial subsets, for all *maximal* $k > (n/2)$ rank mappings, which are compatible with the use of $\lambda \vdash n$ weak-partitional branching in SFP, or SF decompositions. Thus, in terms of RSS SF-decompositions over SF basis as in equation (23a), one finds that

$$\begin{pmatrix} 1 \\ 23 \\ 252 \\ 1748 \\ 8602 \\ 31878 \\ 96092 \\ - \end{pmatrix} \begin{pmatrix} 1 \\ 39 \\ 740 \\ 9100 \\ 81510 \\ 566618 \\ 3180572 \\ \dots \end{pmatrix} : \sum_v T^{k'}(v)$$

$$\equiv \begin{pmatrix} 1\;0\;0\;0; & & & & \\ \bar{1}\;2\;0\;0; & & & & \\ 0\;\bar{1}\;2\;1; & & & & \\ 0\;\bar{1}\;\bar{2}\;1; & 2\;2\;0; & & & \\ 0\;0\;1\;0; & \bar{2}\;0\;1; & 2\;2\;1\;0\;0; & & \\ 0\;0\;\bar{1}\;0; & 0\;0\;\bar{1}; & \bar{2}\;0\;\bar{1}\;2\;0; & 2\;2\;2\;0; & \\ (0\;0\;0\;0; & 1\;\bar{2}\;0; & 0\;\bar{2}\;2\;\bar{1}\;0; & \bar{2}\;0\;\bar{2}\;2\;1\;0; & 2\;2\;1\;0\;1) \\ \dots; & \dots; & \dots; & \dots & \end{pmatrix} \widehat{\mathcal{L}}_{RS}, \quad (27)$$

where the negative entries arise solely from the rank-alone construction, which recursively subtracts *just the full positive component* SFPs of the preceeding k-rank $\mathcal{Z}_{i-1}$ result in the hierarchy – on proceeding in a stepwise manner from the maximal rank, as set out in equation (26).

This matrix of SF-coefficients is based on the SR properties of specific bipartite SF products, equations (19)–(22). The rank-alone tensorial subset dimensionality (on the left in equation (27)) derives from the recursive combinatorial property

$$\chi^{2n-i,i}_{1^{2n}}(\mathcal{S}_{2n}) \equiv \binom{2n}{i} - \binom{2n}{i-1}. \quad (28)$$

The full (spin-alone) tensorial set has a spatial dimensionality of $\binom{2n}{n}$; this follows directly from a further straightforward combinatorial identity. On utilising the full range of single SF YR-III decompositions (in the weak part branching limit), one obtains a mapping (for tensorial ranks) onto the $\{[\widetilde{\lambda}]\}$ irrep space of the $\mathcal{S}_n$ group. Here again the entries are in terms of decreasing rank, with the dominance ordering (over irreps) retained in the right-hand $\mathcal{L}(\mathcal{S}_n)$ column-vector. Finally, as a specific example for the tensorial forms of the $n = 12$ index symmetric group (or as outer portions of higher $\mathcal{S}_{n>12}$ groups), one obtains the following overall *maximal* form:

$$\begin{pmatrix} i=0 \\ 1 \\ 2 \\ 3 \\ 4 \\ 5 \\ \dots \end{pmatrix} : \sum_v \quad T^{k_{\max}-i}(v) \equiv \begin{pmatrix} 1\ 0\ 0\ 0; & & & \\ 1\ 2\ 0\ 0; & & & \\ 2\ 3\ 3\ 1; & & & \\ 2\ 5\ 5\ 3; & 4\ 2\ 0; & & \\ 3\ 6\ 9\ 4; & 7\ 6\ 1; & 5\ 3\ 1\ 0\ 0; & \\ 3\ 8\ 11\ 6; & 13\ 10\ 1; & 9\ 9\ 3\ 2\ 0; & 6\ 4\ 2\ 0 \\ (\dots) & & & \end{pmatrix} \mathcal{L}(\mathcal{S}_n). \tag{29}$$

This concludes the essential details of the derivation of the full carrier space maps down to $k = (n/2) \equiv 6$, for the $n = 12$ dual group.

4. Simple reducibility and subspatial partitioning

From the initial discussions of the structure of equation (6), Liouvillian carrier space is known to be partitionable [53,55,60]. Thus, the distinct auxiliary labels (being precisely $n-2$ (recoupling) labels, from an "n"-fold k_i inner field) provide a structured series of subsets mappings based on the underlying scalar invariants, with

$$\sum_v T^{k'}(v : \mathcal{S}_n) \equiv (\dots)_{\bar{v}} + (\dots)_{\bar{v}'} + \cdots. \tag{30}$$

It is this property which ensures the retention of SR property of $SU(2) \times \mathcal{S}_n$ Liouville space, as in [53,55,60]. Over irrep-basis set out in equation (23b), the initial v-term-based matrix is given by

$$T^{k_{\max}-i}(\bar{v}) \equiv \begin{pmatrix} 1\ 0\ 0\ 0; & & & \\ 1\ 1\ 0\ 0; & & & \\ 1\ 1\ 1\ 1; & & & \\ 1\ 1\ 1\ 1; & 1\ 1\ 0; & & \\ 1\ 1\ 1\ 1; & 1\ 1\ 1; & 1\ 1\ 1\ 0\ 0; & \\ 1\ 1\ 1\ 1; & 1\ 1\ 1; & 1\ 1\ 1\ 1\ 0; & 1\ 1\ 1\ 0 \\ (\dots) & & & \end{pmatrix}^{\bar{v}} \mathcal{L}(\mathcal{S}_{12}). \tag{31}$$

The remaining SR subsets are suitable fragments of the residual matrix; for the present high k-rank weak-branching case, this further (for compactness of the presentational

Table 1
Illustrative enumeration of T^k dual tensor decompositions: the case of $\mathcal{Z}_4 - \mathcal{Z}_3$ skew-diagonal sum difference, from lefthand (NW) corner of figure 1.

Dimension			Coefficients/$\{[\widetilde{\lambda}]\}$	[3]	[21]	[111]	[4]	[31]	[22]
	$\{\widehat{22}\}$	$\rightarrow$	1 2 3 1;	2	2	0;	1	1	1
	$2\{\widehat{31}\}$		2 4 4 2;	4	2	0;	2	2	
	$2\{\hat{4}\}$		2 2 2 0;	2		;	2		
	$\{\widehat{111}\}$		1 3 3 3;	1	2	1;			
	$2\{\widehat{21}\}$		2 4 4 2;	2	2				
	$\{\hat{2}\}$		1 1 1 0;						
10626	$\sum$	$=$	9 16 17 8;	11	8	1;	5	3	1
2024	$2(\{\widehat{21}\} + \{\hat{3}\} + \{\widehat{11}\})$	$=$	6 10 8 4;	4	2				
8602	Δ	$=$	3 6 9 4;	7	6	1;	5	3	1

Table 2
A further enumerative decomposition which illustrates the case of $\mathcal{Z}_5 - \mathcal{Z}_4$.

Dimension			Coefficients/$\{[\widetilde{\lambda}]\}$		[4]	[31]	[22]	[211]	[5]	[41]	[32]
	$2\{\widehat{32}\}$	$\rightarrow$	2 4 6 2;	6 4 0;	4	4	2	0 0;	2	2	2
	$2\{\widehat{41}\}$		2 4 4 2;	4 2 0;	4	2	0	0 0;	2	2	
	$2\{\hat{5}\}$		2 2 2 0;	2 0 0;	2	0	0	0 0;	2		
	$2\{\widehat{211}\}$		2 6 8 6;	6 8 2;	2	4	2	2 0;			
	$2\{\widehat{31}\}$		2 4 4 2;	4 2 0;	2	2	0	0 0;			
	$2\{\widehat{21}\}$		2 4 4 2;	2 2 0;							
42504	$\sum$	$=$	12 24 28 14;	24 18 2;	14	12	4	2 0;	6	4	2
10626	$\mathcal{Z}_{i-1}$	$=$	9 16 17 8;	11 8 1;	5	3	1	0 0;			
31878	Δ	$=$	3 8 11 6;	13 10 1;	9	9	3	2 0;	6	4	2

layout herein) composite component mapping is given by

$$\sum_{v=\bar{v}'}^{\bar{v}'',\ldots} T^{k_{\max}-i}(v) \equiv \left(\begin{array}{lllll} 0\ 0\ \ 0\ 0; & & & & \\ 0\ 1\ \ 0\ 0; & & & & \\ 1\ 2\ \ 2\ 0; & & & & \\ 1\ 4\ \ 4\ 2; & 3\ 1\ 0; & & & \\ 2\ 4\ \ 8\ 3; & 6\ 5\ 0; & 2\ 4\ 0 & & \\ 2\ 7\ 10\ 5; & 12\ 9\ 0; & 8\ 8\ 2\ 1\ 0; & 5\ 3\ 1\ 0 & \\ (\ldots) & & & & \end{array} \right)^{\bar{v}',\bar{v}'',\ldots} \mathcal{L}. \tag{32}$$

Naturally, each of the SR component submatrices is associated with a specific v-invariant derived from hierarchical group chain [17,49,60] structures, as developed in the following paper [62] which treats the complete $\{[\widetilde{\lambda}] \mid p \leqslant 4 \text{ part } : \mathcal{S}_{12}\}$ irrep set.

The derivation of a specific k-rank $T^k(v)$ versus $\{[\widetilde{\lambda}]\}$ map, i.e. as an example of one specific row of equation (29), follows directly from equation (27) and from the use of YR-III rule; for details the reader is referred the enumerations given respectively in tables 1 and 2, where again the negative components are those derived from a preceeding tensorial subset in the recursive process, this being just the respective postive $\mathcal{Z}_{i-1}$ (sum) contribution (i.e. *without* the earlier subtraction being applied).

5. Discussion

It has been convenient to focus on the higher rank properties with their *maximal* forms of *bipartite* SF inner products, under the previously stated $\lambda \vdash n$ weak-branching criteria. The other subset rank-alone mappings, i.e. those for which $k \leqslant n/2$, are more tedious to calculate, since their component forms are *no longer* generalised (higher n-index independent) inner SFP mappings, neither do they exhibit analogous forms to equations (19)–(22). However, proofs of both the $k > n/2$ and, rather more tediously, the $k \leqslant n/2$ forms of tensorial components may be obtained in principle via the SYMMETRICA symbolic computing package [35] and its associated $\mathcal{S}_{12}$ (or $\mathcal{S}_{20}$) group algebras. The technique adopted here has allowed a fuller realisation of the $\widetilde{\mathbb{H}}_v$-based SR properties of *SU*(2)$\times\mathcal{S}_n$ dual group tensorial sets of value in treating, e.g., spin-(1/2) ensemble NMR dynamics, as they arise in evolution, coherence transfer, or intracluster relaxation phenomena.

These SR properties arise as a result of factorisation associated with the auxiliary v labels, and hence SI terms, which are now an explicit feature of the projective mapping, as compared to their ancillary role in Biedenharn and Louck state-space formalism [9,10]. It should be noted that the tensorial subsets were obtained utilising almost exclusively the symmetric group algebra – the usage of unitary group aspects here was limited specifically to defining the range of parts (p) for the $\lambda \vdash n$ forms. The role of the symmetric group is central also in defining the sub-spatial dimensionalities, via the appropriate $\chi^{[2n-i,i]}_{1^{2n}}(\mathcal{S}_{2n})$ characters. The $\mathcal{S}_n$-democratic recoupling associated with the realisation of scalar invariants (SIs) is the subject of a following paper [62], which utilises the properties of the Yamanouchi chain to resolve a major analytic weakness inherent in many-body (democratic) recoupling problems.

Whilst the democratic approach to recoupling yields an analytic way of treating one of the strictly few-body cases, via the explicit algebraic quantum physics first given by Lévy-Leblond and Lévy-Nahas [37] in l965, the generalised problem is not tractable in terms of conventional analytic forms for theoretical reasons. A proof of this *intrinsic* intractability, i.e. for highly degenerate systems based on descriptions involving *multiple scalar invariants*, was given via group theory initially by Galbraith [23]. Little progress seemed possible thereafter, at least until the $\widetilde{\mathcal{V}}$ forms of v labels were reformulated in terms of the combinatorially-based $\mathcal{S}_n$ group YGC chain process. These route-maps, essentially onto [2]($\mathcal{S}_2$), are discussed in detail in the following paper [62].

As well as allowing a viable approach to coherence transfer of a small number of $[A]_n$-type spin systems [38], it is noted that the dual group viewpoint allows one to define *symmetry breaking* in NMR, as being associated [38] with, e.g., the $\phi^1_1(11)$, or more generally, the $\phi^{n-1}_{n-1}(1_1, \ldots, 1_n)$) coherences, which are inherently disallowed for evolution under the zeroth-order Liouvillian.

Studies of evolution involving *penultimate maximal quantum* processes of multispin systems, under scalar coupling, or in particular dipolar, Liouvillians yield much physical insight, as given, e.g., in a recent liquid crystal media NMR report [14] describing phase-selective specific multiquantum COSY NMR of $[A]_4(\mathcal{S}_4 \downarrow \mathcal{D}_2)$ systems. This succeeded in extending Avent's technique [2], which was originally applied to an isotopic dipolar $A[B]_3$ spin system (in liquid-crystal media) in the 1980s. However, one should note that the discrimination employed therein does not allow for pairs of distinct highly degenerate $[\widetilde{\lambda}]$s to be distinguished directly *a priori*, i.e. where they share the *same q (multiquantum) manifold*. Hence this early pulse technique employed in [14] may be of somewhat limited value in NMR applications, where the original intention is to identify spectral features belonging to different highly degenerate irreps in similar q subspaces under (say) some $\mathcal{S}_{n\geqslant 6}$-related group. To date, the further interesting question of correlating NMR features with specific invariants has not received much attention, in part for the reasons indicated above. Since the high-resolution liquid state NMR community has tended to avoid the use of recoupled tensorial formalisms in treating the spin dynamics of *multispin* systems, by choosing instead to focus on techniques involving product (or generalised unitary projective) bases. Work involving these bases frequently neglects the recoupling aspects inherent in NMR altogether. Except for the pedagodical Hilbert space discourse on the number of independent SIs, due to Corio [20], little mention has been made of SIs in modern NMR; the explicit role of multiple SIs over a Liouvillian carrier space has not been considered by others previously, and certainly not in the detailed form addressed here and in the following work [62].

6. Concluding remarks

The dynamical formalisms of NMR based on dual-group tensorial sets are invaluable in understanding the physical role of scalar invariants as auxiliary terms. Further, the completeness of the sets associated with projective mapping provides direct insight into dual group transformational properties of Liouville space. Many of the general techniques invoked here, such as those based on Schur functions, stress the value in molecular physics of the $(SU(2)\times)\mathcal{S}_n$ group [6,26,39,50]. The concept of simple reducibility [53,55,60] is of special importance under this dual group, as shown previously in [53,55]. The inclusion of other group theoretical approaches – including those frequently associated with other specific areas of physics [50] – often proves helpful. Here, it has been shown that theoretical techniques, based on SFs from atomic [12,13,68] and particle physics [48,49], are also of pertinence to chemical physics and to modern-day NMR [45,60,62].

Even leaving aside the group structural aspects of equation (14), the necessity of retaining the $\mathcal{S}_n$ group in NMR, as in [55], is clear from the involvement of wreathproduct groups in molecular dynamics, involving spins, i.e. under the so-called "feasibility group"), as explored by Longuet-Higgins [39] and (more recently) by Balasubramanian [6]. Explicit use of $\mathcal{S}_n \downarrow \mathcal{G}$ natural embeddings in CNP studies are now a well-established aspect for the nuclear spin statistical weighting of ro-vibrational spectroscopy [3–5,8,26,56,57,66]. The relationship of such processes to other common subductions (i.e. those based on the orthogonal group) [1,11,16,25,27] comes directly from equation (14a). The distinction between spin-based CNP presentations [5,8,26,66] and purely vibrational analyses of cage structures [16,27] is clear from the nature of the constrained total CNP/spin-vibrational product symmetry and is well-established in terms of chemical applications in the spectroscopic literature [4,11].

The techniques presented here for deriving the inherent structure of dual tensorial sets goes significantly beyond the restricted (circa) 4- or 5-fold tensorial sets, based on the earlier $(\otimes SU(2))^n$ notation due to Coope [22], or indeed that of other tensorial approaches, such as that due to Hughes [28,69]. Within the context of Liouville space itself being a product space, the additional symmetry chain

$$SO(5) \supset SU(2) \times SU(2)$$

is of interest to NMR spin dynamics, because it is directly related to the Hilbert space viewpoint adopted by Corio [20].

The use of dual group carrier space based techniques allows highly degenerate systems (not necessarily restricted to NMR) to be treated via democratic recoupling [55,60,62] in a way that is conceptually insightful and compatible with other projective techniques [64,65], and also (to some extent) with theories associated with networks, whether these are based on equivalence hierarchies and automorphisms [3], or else via interlink modelling which may be found in descriptions of "small-world" networks [67]. For higher n-fold ensembles, there is clearly a *disjunction* between conventional tree-based graphical techniques [33,41] and $\mathcal{S}_n$ projective techniques, in regard to transformations between the two formalisms for multiple scalar invariant problems; this is not as widely appreciated in the physical science as it deserves to be. As a well-defined application of symbolic algebraic combinatorics to chemical physics, in the context of [53,55,60] and related articles [62–64], the work could well be of interest outside the confines of NMR spin dynamics.

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Appendix

It should be noted that the square construction of figure 1 is based on each of the component quadrants, $(--), (-+), (+-), (++)$, being a Latin square.

Isometry between $\mathcal{GL}_n$, $\mathcal{S}_n$ groups also applies to outer products derived by Littlewood–Richardson rule with its lattice permutation criteria. Details may be found in the appendix C material of Sternberg's text [48] and in sections I, II of the discussion of "splitting the square" (outer plethysm formation) recently given by Carré and Leclerc [15]. Explicit $[\lambda] \otimes [\lambda']$ IP decompositions using the techniques of equations (12)–(15) and the $\mathcal{S}_n \otimes \mathcal{S}_n \rightarrow \mathcal{S}_n$ for $n = 12$, and $20 \leqslant n \leqslant 24$ symbolic computation with SYMMETRICA has been presented in our recent work [60].

Since tabulations of simple YR-III SF decompositions (onto $\{[\lambda]\}$ space) have been extensively treated in earlier work [54,58,59,61,63], and in any case the algorithmic form [40] is particularly straightforward, these aspects are not set out here. Suffice it to say that the *maximal* forms of such enumerations have been utilised for YR-III, as well as for the restricted space SF product mappings. Further detailed discussion of notation, and of some of the historical background on the earlier mathematical contributions (in terms of (outer) plethysms) of Murnaghan and of Littlewood (i.e. from circa 1936 up to 1958), may be found in Butler's work [12,48] from the 1970s.

References

[1] R. Ahlrichs and S.D. Elliott, Phys. Chem. – Chem. Phys. 1 (1999) 13.
[2] A.G. Avent, J. Magn Reson. 53 (1983) 513.
[3] K. Balasubramanian, J. Chem. Phys. 78 (1983) 6358, 6369.
[4] K. Balasubramanian, Chem. Rev. 85 (1985) 599.
[5] K. Balasubramanian, Chem. Phys. Lett. 183 (1991) 292; 197 (1992) 55.
[6] K. Balasubramanian, J. Chem. Phys. 95 (1991) 8273.
[7] K. Balasubramanian, J. Phys. Chem. 97 (1993) 4647.
[8] K. Balasubramanian, K.S. Pitzer and H.L. Strauss, J. Mol. Spectrosc. 93 (1982) 447.
[9] L.C. Biedenharn and J.D. Louck, *The Permutation Group in Physics and Chemistry* (Springer, Heidelberg, 1979).
[10] L.C. Biedenharn and J.D. Louck, *Angular Momentum Theory in Physics; Racah–Wigner Algebra*, Vols. 8, 9 (Cambridge University Press, Cambridge, 1981/1985).
[11] P.H. Bunker and P. Jensen, *Molecular Symmetry and Spectroscopy* (NRC, Ottawa, 1998).
[12] P.H. Butler, J. Phys. (Paris) 31/C4 (1970) 47.
[13] P.H. Butler and R.C. King, J. Math. Phys. 14 (1973) 1176.
[14] J. Carravella, F. Castilione, G. Di Luca, J.W. Emsley, J.C. Lindon, M. Longeri, W.E. Palke and D.L. Turner, J. Magn. Reson. 135 (1998) 298.
[15] C. Carré and B. Leclerc, J. Algebraic Combin. 4 (1994) 201.
[16] A. Ceulemans, P.W. Fowler and I. Vos, J. Chem. Phys. 100 (1994) 5491.
[17] J.Q. Chen, *Group Representation Theory for Physicists* (World Scientific, Singapore, 1987).
[18] J.A.R. Coope, J. Math. Phys. 11 (1970) 1591.
[19] P.L. Corio, *The Structure of High-resolution NMR Spectra* (Academic, New York, 1967).
[20] P.L. Corio, J. Magn. Reson. 134 (1998) 131.
[21] P. Diehl and C.L. Khetrapal, Principles, Progr. NMR 1 (1969) 1.
[22] U. Fano and G. Racah, *Tensorial Sets* (Wiley, New York, 1959).

[23] H.W. Galbraith, J. Math. Phys. 12 (1972) 782.
[24] M. Goldman, *Quantum Description of High-resolution NMR in Liquids* (Oxford University Press, Oxford, 1988).
[25] W.G. Harter, *Principles of Symmetry, Dynamics and Spectroscopy* (Wiley, New York, 1994).
[26] W.G. Harter and T.C. Reimer, Chem. Phys. Lett. 198 (1994) 429.
[27] W.G. Harter and D.E. Weekes, J. Chem. Phys. 90 (1989) 4727.
[28] J.B. Hughes, J. Math. Phys. 24 (1983) 1015.
[29] G.D. James and A. Kerber, *Representations of the Symmetric Group* (Cambridge University Press, Cambridge, 1981).
[30] R.G. Jones, Principles, Progr. NMR 1 (1969) 100.
[31] R.G. Jones, R.C. Hirst and H.J. Bernstein, Canad. J. Chem. 43 (1965) 683.
[32] R.G. Jones and S.M. Walker, Molecular Phys. 10 (1965) 349.
[33] A.P. Jucys, I.B. Levinson and V.V. Vanagas, *Mathematical Theory of Angular Momentum* (Israeli Translation Program, Jerusalem, 1963).
[34] A. Kerber, *Combinatorics via Finite Group Actions* (BWI, Mannheim, 1991).
[35] A. Kohnert, A. Kerber and A. Lascoux, J. Symbolic Comput. 14 (1993) 195.
[36] V. Krishnamurthy, *Combinatorics, Theory and Applications* (E. Horwood, Chichester, 1988).
[37] J.M. Lévy-Leblond and M. Lévy-Nahas, J. Math. Phys. 6 (1965) 1372; 7 (1966) 2217.
[38] J. Listerud, S.J. Glaser and G.P. Drobny, Molecular Phys. 78 (1993) 629.
[39] C.H. Longuet-Higgins, Molecular Phys. 6 (1963) 445.
[40] B.E. Sagan, *The $\mathcal{S}_n$ Group, Its Representations, Combinatorial Algorithms and Symmetric Functions* (Wadsworth Math., Pacific Grove, 1991).
[41] B.C. Sanctuary, J. Chem. Phys. 64 (1976) 4352.
[42] B.C. Sanctuary, J. Magn. Reson. 61 (1985) 116.
[43] B.C. Sanctuary, Molecular Phys. 55 (1985) 1017.
[44] B.C. Sanctuary and M.S. Krishnan, J. Magn. Reson. 69 (l986) 210.
[45] B.C. Sanctuary and T.K. Halstead, Adv. Opt. Magn. Reson. 15 (1991) 97.
[46] B.C. Sanctuary and F.P. Temme, Molecular Phys. 56 (1985) 1049.
[47] H.W. Spiess, Principles, Progr. NMR 15 (1978) 58.
[48] S. Sternberg, *Group Theory in Physics* (Cambridge University Press, Cambridge, 1994).
[49] J.J. Sullivan, J. Math. Phys. 24 (1983) 2542.
[50] J.J. Sullivan and T.H. Siddall-III, J. Phys. Chem. 96 (1992) 5789; J. Math. Phys. 33 (1992) 1964.
[51] F.P. Temme, Chem. Phys. 32 (1989) 9.
[52] F.P. Temme, J. Magn. Reson. 83 (1989) 383.
[53] F.P. Temme, Physica A 166 (1990) 676.
[54] F.P. Temme, Z. Phys. B 88 (1991) 83; 89 (1992) 332.
[55] F.P. Temme, Physica A 198 (1993) 245.
[56] F.P. Temme, Coord. Chem. Rev. 143 (1994) 1169.
[57] F.P. Temme, Physica A 210 (1994) 435; 202 (1994) 595.
[58] F.P. Temme, Molecular Phys. 85 (1995) 883; 86 (1995) 981.
[59] F.P. Temme, J. Math. Chem. 21 (1997) 373; 24 (1998) 133.
[60] F.P. Temme, Chem. Phys. 238 (1998) 245.
[61] F.P. Temme, Eur. Phys. J. 11 (1999) 177.
[62] F.P. Temme, J. Math. Chem. 27 (2000) 131 (this issue).
[63] F.P. Temme, Canad. J. Phys. (2000) (to be published).
[64] F.P. Temme, J. Magn. Reson. (2000) (to be published).
[65] F.P. Temme, Int. J. Quantum Chem. 78 (2000) 71.
[66] F.P. Temme, C.J.E. Mitchell and M.S. Krishnan, Molecular Phys. 79 (1993) 953.
[67] D.J. Watts, *"Small-Worlds": The Dynamics of Networks between Order and Randomness* (Princeton University Press, Princeton, NJ, 1999).

[68] B.C. Wybourne, *Symmetry Principles in Atomic Physics* (Wiley, New York, 1970).
[69] B.G. Wybourne, J. Phys. (Paris) 31/C4 (1970) 33.
[70] M. Ziauddin, Proc. London Math. Soc. 42 (1936) 340.