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Multipole N.M.R.

XIII. multispin interactions and symmetry in Liouville space

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The multipole formulation of N.M.R., as applied to multi-spin systems, makes use of a basis that is composed of rotationally invariant tensor operators. For spin systems that have magnetic symmetry, it is possible to adapt this Liouville space into a basis which is also irreducible under the appropriate permutation symmetry. This permits a systematic treatment of the various multiquantum spectra and leads to a dramatic factorization of the Liouville matrix. Examples of AA' and $AA'BB' \equiv [AB]_2$ systems are included as illustrations. The effect of introducing the weak coupling limit is shown to further reduce the dimensionality of submatrices for the related $[AX]_2$ system.

1. INTRODUCTION

The use of rotational invariance in treating problems in spin dynamics leads to a systematic and general description of multiquantum pulsed N.M.R. Most of the advantages stem from the development of Racah algebra associated with the use of multipole bases that are spherical tensors operators, irreducible under the rotation group. With the additional techniques used in treating differential equations, this approach to the time evolution problems of spin dynamics avoids the evaluation of cumulative commutators. Indeed, once a single commutator has been evaluated, it provides a totally general method of solving a range of pulsed N.M.R. problems [1–4]; it yields analytical results that in most instances are exact, and has some additional uses in the field of N.Q.R. [5]. For hamiltonians involving single spins in external fields, the relationship between multipoles and spherical harmonics has given rise to a visual interpretation [6] of the nature of spin polarizations.

For multispin interactions in multiquantum domains, the problem of the 'internal' field exerted by one nuclear spin interacting with another via scalar coupling is rather more involved than the original applications of multipole theory. Aspects of an additional formalism, namely the multispin basis $T^{kq}(v)$ required to treat scalar coupling, has been used previously in the context of relaxation theory [7]. Different aspects of the two spin case are discussed using this basis in two closely related papers; the first publication [8] traces the causes of scalar coupling to certain normally unobservable polarizations. A subsequent paper [9] investigates the mechanism of decoupling in terms that involve the treatment of time evolution by the use of Laplace transforms [10]. Consideration

of the complete set of polarizations is essential in such problems. The present paper deals with more general multispin systems with particular reference to the question of how symmetry may be used to assist the solution of the (isotropic) scalar coupling hamiltonian and its time evolution in the strong and weak coupling limits. A general method for generating specialized multipole bases that are irreducible under the appropriate (magnetic) point group is given and shown to be particularly useful for spin systems involving magnetic inequivalence of the form, $AA'BB' \equiv [AB]_2$, or more generally, such as $AA'A'' \ldots MM'M'' \ldots XX'X' \ldots \equiv [AMX]_n$, etc.

One reason for the choice of a particular basis in which to treat multispin scalar coupling problems has been the need to retain f^z as an eigenoperator [11] of the Liouville $|kq\rangle\rangle$ basis set [12]. Such a choice provides a maximum initial block diagonalization of the Liouville matrix. For these hamiltonians q constitutes a good quantum number; however, not all hamiltonians are so well-behaved. In particular, those which involve additional I_+^n terms such as hamiltonians involving rf radiation [13], render the Liouville operator and f^z non-commuting, and q inadmissible as a quantum number.

A particularly serious problem in the treatment of multispin systems in Liouville space is the large dimensionality of the corresponding matrix, namely $\Pi_{i=1}^n (2I+1)^2$ compared to $\Pi_{i=1}^n (2I+1)$ for Hilbert space. Whilst there have been many applications of symmetry to conventional vector space problems [14–19], no general method of using such techniques in Liouville space has previously appeared. The present paper uses projection operator techniques to produce an operator basis that is irreducible under the pertinent permutation symmetry. The formal equivalence between symmetry adaptation using projection operators and symmetrizing basis vectors is well known [14, 20].

Naturally, there will be systems which lack symmetry and for which no additional factorization of the Liouville matrix is possible. Even so, consideration of higher q domains without additional symmetry leads to useful experimental algorithms, such as network analysis [21]. Other simplifications, such as used by Bain [22] in his superspin formalism, are applicable to ABX-like systems. A recent pedagodical comparison [12] of Liouville, Hilbert and other spaces, compares and contrasts descriptions of such spaces. This provides a consistent nomenclature for basis sets in different spaces and is readily related to earlier treatments [11, 23–28].

Section 2 of this paper gives a formal description of the time evolution of multispin systems involving scalar coupling; it uses some of the criteria for basis selection discussed in the paper just mentioned [12]. Section 3 is concerned with the general projection operator technique for generating a specialized multipole operator basis which is symmetry-adapted to a specific point group; it shows how this leads to a significant reduction in the dimensional order of the Liouville matrix for large multispin hamiltonians. The particular problem examined, as an example of this perfectly general technique, is that of the four spin $[AB]_2$ (or in the older terminology, $AA'BB'$) system in multiquantum space under C_2 symmetry. The basis that results from symmetry adaptation is summarized in table 4. Extension of the technique to other clusters of like I spins subject to particular inherent (magnetic) symmetry is possible. Additional implications of the nature of coupling are discussed more fully in §3. In §4 and table 5 the effects of using a weak coupling limit are considered.

2. General multispin interactions

The purpose of using symmetry in quantum mechanical problems is to reduce the dimensionality of the hamiltonian representations by symmetry factorization. In Hilbert space one chooses a basis which reduces the dimensionality as much as possible by choosing [14],

(1*a*) total magnetic quantum number, $m_t = F_z = \sum_i m_i$,

(2*a*) total spin quantum number I_t, and

(3*a*) symmetry factorization of Hilbert space.

The same motivation and possibilities exist in Liouville space by choosing,

(1*b*) total qth spherical component, $q = \sum_i q_i = \sum_i (m_i' - m_i)$,

(2*b*) the total multipole character (tensor rank), k,

(3*b*) symmetry factorization of Liouville space.

Items (1*a*) and (2*a*) result in the standard state basis $|I_t m_t \alpha\rangle$ while (3*a*) symmetry adapts these under some appropriate point group to $|I_t m_t \alpha\rangle_\mu$.

Items (1*b*) and (2*b*) are the parallel motivation for choosing a multipole basis, $|kqv\rangle\rangle = T^{kq}(v)$, where q describes the qth quantum spectrum, (Bain [26] calls his basis superspin). Item (3*b*), which provides the emphasis of this paper, imposes additional point group symmetry contraints and leads to further factorization in sense, $|kqv\rangle\rangle_\mu$.

Earlier formal treatments of coupled spins [7, 29] have defined the construction of operators to span $\Pi_{i-1}^{n}(2I+1)^2$ space for n interacting spins based on (1*b*) and (2*b*). Such bases are not so simple to specify as those for treating a single nuclear spin. Conventional descriptions of coupled systems, however, imply certain specific constraints on the form of spin interaction; thus, AA', A_2X and ABX correspond respectively to a symmetry, a purely magnetic, and a so-called X constraint on coupling. The salient difference for example between ABC and AMX spin systems, cf. figure 1 (ii), lies in the importance of combination terms [25] leading to a single q being a good quantum number for the ABC case; by contrast, in AMX all the q_i(for $i = A$, M, or X) are good quantum numbers.

In general the formal multipole basis operator set for an n spin system, using only (1*b*) and (2*b*) above, is

$$T^{kq}(v) = T^{kq}_{\{\bar{K}\}}(k_1 \ldots k_n), \tag{1}$$

where for brevity the generic label v is used for the k_i set of n spins that span

$$0 \leqslant k_i \leqslant 2I_i \tag{2}$$

and cause a specification of $2n-2$ intermediate Racah coupling parameters $\{\bar{K}\}$. This form focuses on the single resultant entity and its kq values which describes a group of $AA'A'' \ldots A_n$ magnetically equivalent spins. For three spins of $\frac{1}{2}$, the totally coupled basis gives raise to the degenerate multiquantum coherences shown in figure 1 (i). By contrast, the multiquantum coherences produced by three non-equivalent spins of $I_i = \frac{1}{2}$, the ABC, or AMX, case are shown in figure 1 (ii). In calculations, the v terms must impart information on both magnetic equivalence and (for the X approximation cases) the details of any good intermediate q_i parameters. Thus the use of both coupled and uncoupled views of $T^{kq}(v)$

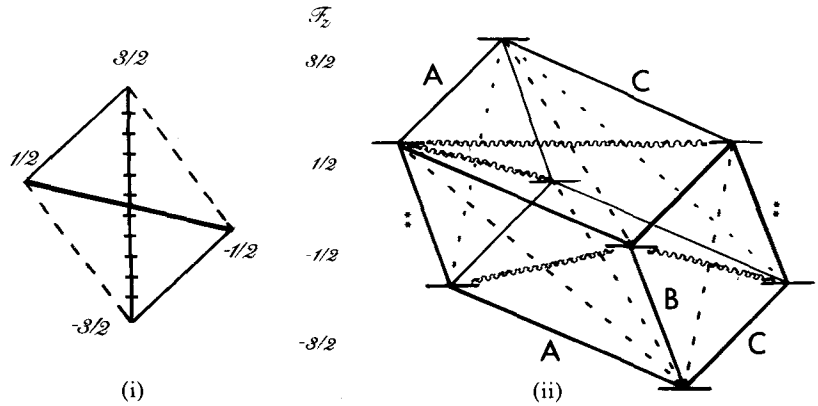

Figure 1. The multiquantum processes in two contrasting three spin-$\frac{1}{2}$ systems under a Zeeman with J-coupling hamiltonian: (i) the coupled A_3 case showing three-fold degenerate $T^{k1}(v)$ (———), two-fold degenerate $T^{k2}(v)$ (– – – –), and the non-degenerate $T^{33}(v)$ (+ + +) coherences. (ii) the ABC spin system corresponding to uncoupled $T^{kq}(v)$ as on the right of (4) of [8] showing 2 of 3 combination $q = 1$ coherences (∗), the six double quanta processes and several illustrative zero quantum coherences (~~~~). For clarity, the $q = 3$ and three inner $q = 1$ coherences are not shown.

operators allow a common framework to exist for the treatment of both A_n and ABC (or AMX) etc. systems. The distinction between such cases is within the specification of the v_i terms.

For an effective two spin problem, say AB_n, the multipole basis takes the form,

$$T^{kq}(k_A, k_B, v_B) = (2I_A + 1)^{-1/2} \sum_{q_A q_B} (-1)^{k_A - k_B + k}(-1)^{k-q} \times \begin{pmatrix} k & k_A & k_B \\ -q & q_A & q_B \end{pmatrix} \mathscr{A}^{k_A q_A}(I_A) T^{k_B q_B}(v_B), \quad (3)$$

where $T^{k_B q_B}(v_B)$ is given by (4) of [8]. Similarly for an $A_m B_n$ system, the multipole basis is

$$T^{kq}(k_A v_A, k_B v_B) = \sum_{q_A q_B} (-1)^{k_A - k_B + k}(-1)^{k-q} \times \begin{pmatrix} k & k_A & k_B \\ -q & q_A & q_B \end{pmatrix} T^{k_A q_A}(v_A) T^{k_B q_B}(v_B). \quad (4)$$

Repeated applications of these equations produce a convenient basis for any spin system, $A_{n_1} B_{n_2} \ldots X_{n_n}$ etc. within the framework described.

The generalized multispin density matrix is

$$\sigma = \sum_{kqv} \phi_q^k(v) T^{kq}(v) \quad (5)$$

and the formal quantum Liouville equation is the set

$$i\hbar \frac{d\phi_q^k(v)}{dt} = \sum_{k'q'v'} \langle\langle T^{kq}(v) | \mathscr{L} | T^{k'q'}(v') \rangle\rangle \phi_{q'}^{k'}(v') \quad (6)$$

Table 1. The uncoupled basis operators for an ABC spin-$\frac{1}{2}$ system. The notation is an extension of earlier $I_A^+ I_B^- I_C^+$, etc., operators of a bilinear treatment, via Lie algebra, which included combination transition operators. The maximum dimensionality is a 9×9 Liouville matrix arising from scalar coupling of type-2 and -3 terms. $n(^{\pm q}_{0})$ denotes the number of such operators. In AMX systems the type-3 operators may be neglected.

Type	Terms of expanded $T^{kq}(v)$ form	Conditions	$+q$	$n(^{+q}_{0})$	$n(^{\pm q}_{0})$
1	$\mathscr{y}^{11}\mathscr{y}^{k0}\mathscr{y}^{k'0}$, etc.	$k' = k = 1$	1	3	
		$k' = k = 0$	1	3	
2	$\mathscr{y}^{11}\mathscr{y}^{k0}\mathscr{y}^{k'0}$, etc.	$k' \neq k$	1	6	30
3	$\mathscr{y}^{1q}\mathscr{y}^{1-q}\mathscr{y}^{1q}$, etc.	$q = 1$ (combination)	1	3	
4	$\mathscr{y}^{k0}\mathscr{y}^{k'-q}\mathscr{y}^{k'q}$, etc.	$k, k' = 0, 1$ $q = 0, 1$	0		20
5	$\mathscr{y}^{k0}\mathscr{y}^{1q}\mathscr{y}^{1q}$, etc.	$q = 1$	2	6	12
6	$\mathscr{y}^{1q}\mathscr{y}^{1q}\mathscr{y}^{1q}$, etc.	$q = 1$	3	1	2

where the v may, in general sense, incorporate additional specification of the spin system, possibly including neglect of higher multipoles in the case of AMX, or other simple product cases. The commutator depends on the specific form of the Liouville operator, $\mathscr{L}A = [H, A]_- \equiv h^{\mathrm{D}}A$, which itself is a reflection of the structure of the hamiltonian—where h^{D} is in the notation of [15]. The commutators necessary for the evaluation of (6) will be found in references [1–10]. The block diagonal nature of many N.M.R. problems arises from the commutation properties of f^z, or equivalently, from the specification of particular q_i as good quantum numbers. In addition, both strong [30] and weak perturbation limits may be used to effectively reduce the number of couplings. The extremely strong coupling case in the A_3 limit is closely related to the $AA'A''$ spin system whose symmetry properties have provided a key to the treatment of strongly coupled ABC systems in Hilbert space [31].

The ideas discussed above indicate that the superoperator descriptions of specific spin systems [11, 13, 25–28] are in a sense subsets of the more general multipole theory [1–10]. With the bases such as those for ABC shown in table 1, the present theory is more general in spanning total multiquantum q space and in its explicit requirement for an initial non-zero polarization to be present in order to observe any possible responses. In most treatments it is usual to retain for a purely static magnetic field only the equilibrium vector polarization. In contrast, our theory incorporates all possible multilinear initial conditions, being the most general extension of a recent description [32].

3. Symmetry factorization

In paper XI the simple case of scalar coupled AB, or AX, spins was treated in detail to show how the multipole theory leads to an extension of the results obtainable from conventional techniques. Banwell and Primas have called the Liouville, or superoperator, approach the direct method whereas treatment in

Hilbert space was denoted the indirect method. In discussing the AB case [11], they restrict consideration to the $q = 1$ components and obtain two 2×2 matrices from their choice of basis as eigenoperators of f_z and of the right-handed $f_{z\mathrm{R}}$ and left-handed $f_{z\mathrm{L}}$ component of f_z superoperators. The fact that (4) of [8] reduces to a quadratic indicates that it is only necessary that the basis be a simultaneous eigenoperator of f_z and not especially of $f_{z\mathrm{R}}$ and $f_{z\mathrm{L}}$. The choice of basis in treating multispin systems, or specific hamiltonians such as that for double resonance [13], is a major factor in obtaining an effective physical description. In addition, as the number of spins increases it becomes important to incorporate additional constraints which leads to further factorization of the hamiltonian matrix. In the indirect approach, Corio [15] has shown that point group symmetry provides an elegant method of achieving this result. He points out the need for F_z to be an eigenoperator of the basis derived from such symmetrization procedures under the (magnetic) point group of the hamiltonian.

Likewise for the direct method, or Liouville approach, it is necessary to choose the spherical tensor operators of the multipole basis to be an eigenoperator of f_z such that,

$$f_z T^{kq}(v) = [F_z, T^{kq}(v)]_- = qT^{kq}(v), \tag{7}$$

where q is simply ΔM. Thus q just labels the multiquantum coherences. When q is a good quantum number there is a corresponding block-diagonalization as discussed for the AB case [11]. In addition, and in general, there are particular advantages in using the $T^{kq}(v)$s namely:

(1) The commutation relations for all the $T^{kq}(v)$s are known for general I_i and any n.

(2) Since a set of differential equations is derived, only one commutator need be calculated.

(3) Since the hamiltonian is of low tensor rank, $l \leqslant 2$, the mixing between the multipole coherences is restricted to those set by the triangular inequality $|k - l| \leqslant k' \leqslant k + l$.

(4) For either weak scalar coupling, or extremely strong coupling, degenerate (or other) perturbation treatments will dramatically reduce the number of couplings etc.

The first three points are dependent on the rotational properties of the multipole basis; the last is particularly apparent when handling for example a set of coupled differential equations in the X approximation of Corio [15].

Alternatively, Cohen [23] has shown that the Liouville matrix $\langle\langle S_{ij}|\mathscr{L}|S_{kl}\rangle\rangle$ elements can be obtained from the hamiltonian matrix elements $\langle\psi_i|\mathscr{H}|\psi_j\rangle$ provided the basis operators S_{ij} obey. $S_{ij}\psi_k = \psi_j\delta_{ik}$. The multipole basis does not obey this property, however.

In addition to (7), spherical tensors obey the relationship,

$$[I_\pm, T^{kq}]_- = \sqrt{[k(k+1) - q(q \pm 1)]}\,T^{kq\pm 1}, \tag{8}$$

which can mix multiquantum coherences. On the other hand, the flip-flop term in scalar coupling, $\{I_+ I_- + I_- I_+\}$, is the origin of mixing of multipole basis components within the same q domain.

In spite of the points (1–4), there still exists a large number of such couplings which cause the dimensionality of the q-sub-domains to be large. These can be

reduced in suitable cases by projecting out specific irreducible components under the appropriate (magnetic) point group. If P_μ is such a projection operator acting on states then,

$$P_\mu |IM\alpha\rangle = |IM\alpha\rangle_\mu . \tag{9}$$

Analogously, Liouville space basis components can be symmetrized by using the corresponding projection superoperator whose projection properties can be formalized to

$$\mathscr{P}_\mu T^{kq}(v) = P_\mu T^{kq}(v) P_\mu^\dagger = T_\mu^{kq}(v). \tag{10}$$

The theory for symmetry-adapting a tensor operator basis by the use of projection operators $\mathscr{P}_\mu$ is formally equivalent to that for symmetrizing basis vectors [14, 20]. It will be noted in passing that the range of application of projection operators with symmetry properties in state space is wide and of continuing interest [33–35].

The actual details of the method are best seen by example. Consider the hamiltonian for an AA' system under C_2 symmetry and initially restrict the basis set to correspond to that for the $I_A = I_{A'} = \frac{1}{2}$, for convenience. The C_2 point group is characterized by the operations E and C_2. Under the identity $\mathscr{E}$ the basis $T^{kq}(v)$ are invarient; in contrast, under the Liouvillian $\mathscr{C}_2$ operation they transform as:

$$\left.\begin{aligned}
\mathscr{C}_2 T^{00}(00) &= T^{00}(00),\\
\mathscr{C}_2 T^{00}(11) &= T^{00}(11),\\
\mathscr{C}_2 T^{1q}(01) &= T^{1q}(10),\\
\mathscr{C}_2 T^{1q}(10) &= T^{1q}(01),\\
\mathscr{C}_2 T^{1q}(11) &= -T^{1q}(11),\\
\mathscr{C}_2 T^{2q}(11) &= T^{2q}(11).
\end{aligned}\right\} \tag{11}$$

These can be deduced either from the tensor properties of the basis as given in table 1 of paper XI, or by applying,

$$\mathscr{C}_2 T^{kq}(11) = C_2 T^{kq}(11) C_2^\dagger \tag{12}$$

to their matrix representations shown in table 2 of the same paper. The matrices $\mathscr{E}$ and $\mathscr{C}_2$ are readily constructed and, in the present specific $I_i = \frac{1}{2}$ case, have traces of 16 and 4, respectively. The number of symmetry-adapted basis operators of $\mathscr{A}$ symmetry may be determined from (using Corio's notation)

$$c_{\mathscr{A}} = \tfrac{1}{2}(16 + 4) = 10,$$

whereas there are

$$c_{\mathscr{B}} = \tfrac{1}{2}(16 - 4) = 6$$

of $\mathscr{B}$ symmetry. Similarly, the projectors,

$$\mathscr{P}_{\mathscr{A}} = \tfrac{1}{2}(\mathscr{E} + \mathscr{C}_2) \tag{13}$$

and

$$\mathscr{P}_{\mathscr{B}} = \tfrac{1}{2}(\mathscr{E} - \mathscr{C}_2) \tag{14}$$

Table 2. The complete set of multiquantum multipole basisoperators $T^{kq}(k_1k_2)$ for the AA', two spin-$\frac{1}{2}$, system symmetrized under C_2 point group. n refers to the number of operators within a specific type, or symmetry designation.

$n_{\mathscr{A}}$	$\mathscr{A}$ $T^{kq}(k_1k_2)$	$\mathscr{B}$ $T^{kq}(k_1k_2)$	$n_{\mathscr{B}}$
1	$T^{00}(00)$		
1	$T^{00}(11)$		
3	$1/\sqrt{2}\{T^{1q}(10) + T^{1q}(01)\} \equiv T^{1q}(\mathscr{A})$	$1/\sqrt{2}\{T^{1q}(10) - T^{1q}(01)\} \equiv T^{1q}(\mathscr{B})$	3
5	$T^{2q}(11)$	$T^{1q}(11)$	3
10			6

applied to the operators give a multipole basis symmetrized under C_2 symmetry. These are listed in table 2 along with their components $(-k \leqslant q \leqslant k)$.

For AA' spin systems with $I_i \geqslant 1$, it is straightforward to extend the basis within the constraint of vector addition and then repeat the processes outlined above; it is noted that the dimensionality problem eventually becomes severe—the $I_i = 9/2$ AA' problem involves $\sim 10^4$ basis operators, for instance. However, for specific $I_i = 1$ case with its 81 basis operators, it is possible to show, from the state space factorization given by Corio [15], that the trace of $\mathscr{C}_2$ is 9 and that the Liouville space factorizes into $\Gamma(\mathscr{A}) = 45$ and $\Gamma(\mathscr{B}) = 36$, as shown in more detail in table 3.

To construct symmetry-adapted bases for more extended spin systems in Liouville space under other groups than C_2, the relationship

$$\mathscr{X}_c T^{kq}(v) = X_c T^{kq}(v) X_c^{\dagger} \tag{15}$$

may be used to construct projection operators. Here $\mathscr{X}_c$ and X_c denote respectively the class c superoperator and operator. For systems other than $AA'A''$

Table 3. The complete $\Gamma_{AA'}$ set, factored into $\Gamma(\mathscr{A})$ and $\Gamma(\mathscr{B})$ representations for multiquantum multipole operator space of AA' under C_2 with $I_A = I_{A'} = 1$. The notation is

$$T^{kq}(ij;\, \mathscr{A}) = 1/\sqrt{2}\{T^{kq}(ij) + T^{kq}(ji)\},$$
$$T^{kq}(ij;\, \mathscr{B}) = 1/\sqrt{2}\{T^{kq}(ij) - T^{kq}(ji)\}.$$

$n_{\mathscr{A}}$	$\Gamma(\mathscr{A})^i$	$\Gamma(\mathscr{B})^i$	$n_{\mathscr{B}}$
9	$T^{4q}(22)$		
5	$T^{2q}(22)$	$T^{3q}(22)$	7
1	$T^{00}(22)$	$T^{1q}(22)$	3
7	$T^{3q}(21;\, \mathscr{A})$	$T^{3q}(21;\, \mathscr{B})$	7
5	$T^{2q}(21;\, \mathscr{A})$	$T^{2q}(21;\, \mathscr{B})$	5
3	$T^{1q}(21;\, \mathscr{A})$	$T^{1q}(21;\, \mathscr{B})$	3
5	$T^{2q}(20;\, \mathscr{A})$	$T^{2q}(20;\, \mathscr{B})$	5
5	$T^{2q}(11)$		
1	$T^{00}(11)$	$T^{1q}(11)$	3
3	$T^{1q}(10;\, \mathscr{A})$	$T^{1q}(10;\, \mathscr{B})$	3
1	$T^{00}(00)$		
45			36

$\ldots \equiv [A]_n$ cases, and particularly for systems involving different groups of equivalent spins, this has two disadvantages. The first was noted by Corio in state space; pure projection alone does not allow the system to exhibit its progression to a weakly coupled form as in $AA'BB' \rightarrow AA'XX'$. A more important point is that, while a single $T^{kq}(v)$ is a natural representation for the totally coupled, $[A]_n$, cases in which symmetry is unbroken and degeneracy is present, there are more appropriate representations for other cases (See figure 1 (i) for an example of the $AA'A''$ case.) In $[A]_n$ cases $T^{11}(v)$ will be ideal as it leads to a single conventionally detectable polarization ϕ_1^1 corresponding to what has been termed equidistant hamiltonians. In other systems, the products of $T^{kq}(v)$s retain the symmetry information, whereby, each elemental operator corresponds to a group of spins with their own symmetry. Consequently, it is possible to retain explicitly all pertinent couplings, and to use them to follow the progression to weak coupling limits. A final comment on the AA' $I_i = \frac{1}{2}$ system concerns the non-magnetic singlet state and the occurrence in table 2 of $T^{11}(\mathscr{B})$ components. In the absence of C_2 symmetry, e.g. AB or AX, no factorization into $\mathscr{A}$ and $\mathscr{B}$ subspaces is needed and all 16 operators mix. Although the $\mathscr{B}$ subspace plays no role for AA' systems, it is important when direct products are formed to generate larger spin systems, e.g. $AA'BB'$ etc.

A useful method of constructing symmetry-adapted multispin bases irreducible under specific point group symmetry is to combine known symmetrized subsystems by a direct product process. This allows the appropriate $\Gamma(\mu)$ to be obtained in both state and operator space for systems such as:

(1) $AA'BB' \rightarrow AA'XX'$.

(2) $AA'A'XX'X''$.

(3) $AA'A''A'''XX'$.

In addition, the effects of imposing a weak coupling limit, as in (1) above, follow once q for each weakly coupled group, is taken as a valid quantum number.

As an example of the above method, table 4 displays the $AA'BB'$ system under C_2 symmetry for $I_i = \frac{1}{2}$, being composed of 256 multipole operators. The direct product processes produced the total symmetry representation $\Gamma_{AA'BB'}$ according to,

$$T_\mu^{kq}(v) \otimes T_{\mu'}^{k'q'}(v') \equiv \sum_{\mu \; \mu'} \Gamma\ (\mu)_{AA'} \otimes \Gamma(\mu')_{BB'} = \sum_{\mu} \Gamma(\mu)_{AA'BB'}. \tag{16}$$

Of these 136 will belong to $\Gamma(\mathscr{A})$ and the remaining 120 to $\Gamma(\mathscr{B})$.

For the equivalent $I_i = 1$ $AA'BB'$ system, it is necessary to classify 6561 components of the basis, which partition into 3321 spanning $\Gamma(\mathscr{A})$ and 3240 within $\Gamma(\mathscr{B})$. For pedagodical purposes, we restrict the treatment to the $I_i = \frac{1}{2}$ case.

When simultaneous factorization under symmetry and q are invoked, it follows that the dimensionality n_q in positive q space under $\mathscr{A}$ symmetry is

$$n_{q=4} = 1; \quad n_{q=3} = 4;$$

$$n_{q=2} = 16; \quad n_{q=1} = 28.$$

whilst in $\mathscr{B}$ space there are one and two 4×4 submatrices, respectively, in $q = 2$ and 1. The dimensions of the factored submatrices approach those of the conven-

tional $AA'BB'$ analysis [16]. It is well known that in symmetrical even–even spin systems there are various reflection properties in the spectra whereas in the odd spin cases under D_3 it is observed that the A and X regions have no such correspondence, e.g. in $[AX]_3$ [17].

Table 4. Complete sets of multiquantum multipole basis operators, $\Gamma(\mu)^i \equiv T^{kq}(v)T^{k'q'}(v')$, for the $AA'BB'$ spin system under C_2 symmetry, showing projection of 136 and 120 operators into the $\mathscr{A}$ and $\mathscr{B}$ domains respectively. The pure $T^{21}(v)T^{k0}(v)$ components are shown as separate features of multiquantum space. The remaining $q = 4$, 3, 2, multiquantum operators ($4q$, tq, dq) correspond to the connected transition processes shown in the energy level diagram, figure 2. The notation for the irreducible representations, $\Gamma(\mu)$, and species, $\mathscr{A}$, $\mathscr{B}$ ... μ of the finite group, $\mathscr{G}$, follow that given by Corio [15].

$(\mathscr{G})_q$ symmetry	$\Gamma(\mu)^i$ basis components	Number of components
$\mathscr{A}_4$	$T^{22}(11)T^{22}(11)$	2
$\mathscr{A}_3$	$T^{22}(11)T^{21}(11)$ $T^{22}(11)T^{11}(\mathscr{A})$	8
$\mathscr{A}_2$	$T^{00}(kk)T^{22}(11)$ $T^{20}(11)T^{22}(11)$ $T^{10}(\mathscr{A})T^{22}(11)$ $T^{11}(\mathscr{A})T^{11}(\mathscr{A})$ $T^{11}(11)T^{11}(11)$ $T^{11}(\mathscr{B})T^{11}(\mathscr{B})$ $T^{11}(11)T^{11}(\mathscr{B})$ $T^{11}(\mathscr{A})T^{21}(11)$	30
$\mathscr{A}_2$	$T^{21}(11)T^{21}(11)$	2
$\mathscr{A}_1$	$T^{21}(11)T^{00}(kk)(k = 0, 1)$ $T^{21}(11)T^{10}(\mathscr{A})$ $T^{21}(11)T^{20}(11)$	16
	$T^{11}(\mu)T^{10}(\mu')(\mu, \mu' = 11, \mathscr{B})$ $T^{11}(\mathscr{A})T^{k0}(11)$ $(k = 0, 2)$ $T^{11}(\mathscr{A})T^{00}(00)$ $T^{11}(\mathscr{A})T^{10}(\mathscr{A})$	32
	$T^{22}(11)T^{1-1}(\mathscr{A})$ $T^{2-1}(11)T^{22}(11)$	8
$\mathscr{A}_0$	$T^{00}(kk)T^{00}(k'k')$ $(k, k' = 0, 1)$ $T^{k0}(11)T^{k0}(11)$ $(k = 1$ or 2, alike$)$ $T^{20}(11)T^{00}(kk)$ $(k = 1, 0)$ $T^{00}(kk)T^{10}(\mathscr{A})$ $(k = 1, 0)$ $T^{10}(\mathscr{B})T^{10}(\mathscr{B})$ $T^{10}(\mathscr{B})T^{10}(11)$ $T^{10}(\mathscr{A})T^{10}(\mathscr{A})$	20
$\mathscr{A}_0$	$T^{1q}(\mathscr{A})T^{1-q}(\mathscr{A})$ $T^{1q}(11)T^{1-q}(\mathscr{B})$ $T^{2q}(11)T^{1-q}(\mathscr{A})$ $T^{1q}(11)T^{1-q}(11)$ $T^{1q}(\mathscr{B})T^{1-q}(\mathscr{B})$ $T^{2,\pm 2}(11)T^{2,\mp 2}(11)$	18
	$\mathscr{A}$ symmetry total,	136

Table 4 (*continued*).

$(\mathscr{G})_q$ symmetry	$\Gamma(\mu)^i$ basis components	Number of components
$\mathscr{B}_3$	$T^{22}(11)T^{11}(\mu)$ $(\mu = 11, \mathscr{B})$	8
$\mathscr{B}_2$	$T^{22}(11)T^{10}(\mu)$ $(\mu = 11, \mathscr{B})$ $T^{11}(\mathscr{A})T^{11}(\mu)$ $(\mu = 11, \mathscr{B})$	16
$\mathscr{B}_1$	$T^{20}(11)T^{11}(\mu)$ $(\mu = 11, \mathscr{B})$ $T^{22}(11)T^{1-1}(\mu)$ $(\mu = 11, \mathscr{B})$ $T^{1q}(\mathscr{A})T^{1q'}(\mu)$ $(\mu = 11, \mathscr{B}; q \neq q' = 1, 0)$	32
$\mathscr{B}_1$	$T^{21}(11)T^{10}(\mu)$ $(\mu = 11, \mathscr{B})$	8
$\mathscr{B}_0$	$T^{00}(kk)T^{10}(\mathscr{B})$ $(k = 1, 0)$ $T^{20}(11)T^{10}(\mathscr{B})$ $T^{10}(11)T^{10}(\mathscr{A})$ $T^{2q}(11)T^{1-q}(\mathscr{B})$ $(q = \pm 1)$ $T^{2q}(11)T^{1-q}(11)$ $(q = \pm 1)$ $T^{1q}(\mathscr{A})T^{1-q}(\mu)$ $(q = \pm 1; \mu = 11, \mathscr{B})$ $T^{00}(kk)T^{10}(11)$ $(k = 1, 0)$	56
	$\mathscr{B}$ symmetry total,	120

Recent two-dimensional dipole–dipole N.M.R. experiments have stressed the importance of connectivity relationships for $AA'BB'$ systems [36]; such relationships for the $q \geqslant 2$ domains are shown in figure 2 for each of the two symmetry subspaces. It is well known that connectivity has its origins in the relative signs of the coupling parameters occurring in the appropriate spin hamiltonian.

Further applications of the $\mathscr{P}_\mu$ operators in the generation of symmetrized Liouville bases spanning q space for other specific spin systems involving clusters of identical I_i spins will be possible. The main difficulty arises from the large number of components involved in such bases. For instance, the six spin-$\frac{1}{2}$ case generates 4096 basis operators. It will be recalled that in Hilbert space several specific six spin-$\frac{1}{2}$ symmetry examples have been treated: ranging from the

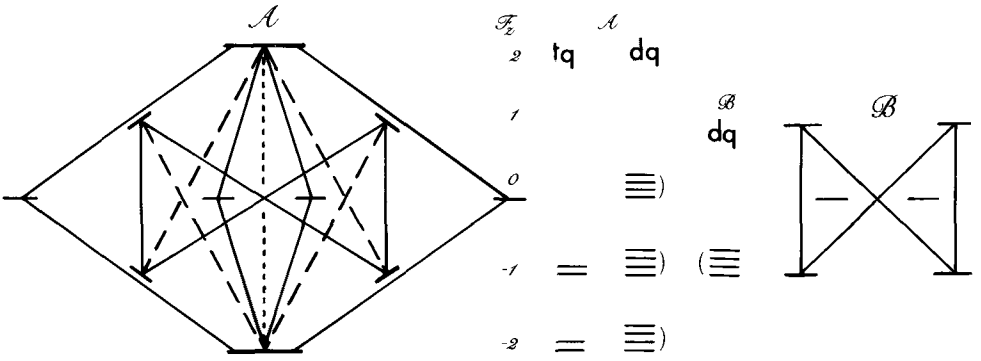

Figure 2. The higher multiquantum coherences of the $AA'BB'$ spin system classified according to symmetry species and F_z. The centre portion of the figure indicates the block dimensionality arising from F_z being a good quantum number. The $q = 1$, 2 and 0 coherences in the $\mathscr{B}$ domain are all doubly degenerate as is a single pair of $\mathscr{A}$ combination operators. The double (dq) and triple quanta (tq) processes are shown as (———) and (– – – –) respectively; the lone $q = 4$ process is denoted (- - - - -).

$AA'A''XX'X'' \equiv [AX]_3$ [17] and $AA'A''A'''XX'$ [37] to a partial treatment of a limiting $AA'BB'XX'$ case [38]. The symmetry aspects in Liouville space of this last system and its $AA'MM'XX'$ derivative will be discussed in future work.

4. X-APPROXIMATION IN SYMMETRIZED SPIN SYSTEMS

In the series, $AA'A''A''' \rightarrow AA'BB' \rightarrow AA'XX'$, the final system is characterized by q parameters derived from the (AA') and (XX') subsystems, in addition to that of the total system, leading to the three good q parameters, $q_{AA'}q_{XX'}$ and $q = \sum_i q_i$, where i runs over all spins. As in state space, this leads to additional factorization, and frequently the dimensions of the resulting submatrices are greatly reduced in all q domains. The specific impact of such parameterization on the present symmetrized spin system in Liouville space is shown in table 5. The

Table 5. The $\Gamma(\mathscr{A})$ and $\Gamma(\mathscr{B})$ representations of $T^{k_{AA'}q_{AA'}}(v_{AA'})T^{k_{xx'}q_{xx'}}(v_{xx'})$ for the $AA'XX'$ system under C_2 group. The $\Gamma(\mathscr{B})$ components are all doubly degenerate which needs to be recalled in accounting for the 120 basis operator belonging to $\Gamma(\mathscr{B})$. Specific v, v' parameters follow from the symmetry classification, as in table 4. The right-hand columns show the double partition of components under symmetry species, μ, and good (XX') quantum number, $q_{(XX')}$. The tabulation refers to n, the dimensionality of the factored $(n \times n)$ submatrices. The label superscript (d) refers to the degeneracy of all components below this point. Table 5 differs from table 4 in the following way. The components listed under headings etc. $\mathscr{A}_q$, $\mathscr{B}_q$ and $q(XX')$ refer to a single space, say positive q values, and not to the sum of components over both $\pm q$ as given in table 4. For corresponding tables in state space for other spin systems, partitioned there by $F_{Z(XX')}$ etc., reference should be made to pages 400–403 of Corio [15], or to Jones [14].

$(\mathscr{G})_q$	$\{\text{total } n(+q)\}_{AA'BB'}$	$\{\text{Typical } \Gamma(\mu)\}^i_{AA'XX'}$	$n_{qXX'}$ for $q(XX') =$				
			-2	-1	0	1	2
$\mathscr{A}_4$	1	$T^{22}(11)T^{22}(11)$					1
$\mathscr{A}_3$	4	$T^{11}(v)T^{22}(11)$					2
						2	
$\mathscr{A}_2$	16	$T^{20}(11)T^{22}(11)$					4
		$T^{11}(v)T^{11}(v)$				8	
		$T^{22}(11)T^{20}(11)$			4		
$\mathscr{A}_1$	28	$T^{2-1}(11)T^{22}(11)$					2
						12	
		$T^{11}(v)T^{10}(v)$			12		
				2			
$\mathscr{A}_0$	38	$T^{2-2}(11)T^{22}(11)$					1
						9	
		$T^{k0}(v)T^{10}(v)$			18		
				9			
		$T^{22}(11)T^{2-2}(11)$	1				
$\mathscr{B}_3$	$2^{(d)}$	$T^{11}(11)T^{22}(11)$					1
						1	
$\mathscr{B}_2$	4	$T^{10}(11)T^{22}(11)$					1
		$T^{11}(\mathscr{A})T^{11}(11)$				2	
					1		
$\mathscr{B}_1$	10	$T^{1-1}(11)T^{22}(11)$					1
						4	
		$T^{11}(11)T^{k0}(\mathscr{A})$			4		
				1			
$\mathscr{B}_0$	28	$T^{1-1}(11)T^{11}(\mathscr{A})$				8	
					12		
		$T^{11}(11)T^{1-1}(\mathscr{A})$		8			

block diagonal substructures in the weak coupling limit, shown to the right of the table, are certainly more tractable than in the original $AA'BB'$ system. It is stressed that orders of submatrices tabulated in tables 4 and 5 arise purely from symmetry and $q(XX')$ considerations. Indeed, these tables are the counter part to the column labelled '$(\mathscr{G})_m$' of table 8.11 of [15] for state space symmetry. Corio [15] also gives exactly equivalent tables in that space for some 6-spin-$\frac{1}{2}$ systems, e.g. tables 8.16 and 8.18.

For the Liouville space $[AB]_2$ and $[AX]_2$ problems, further factorization of a more specific nature will occur from the properties discussed in (A 7) of [8], so that the matrix representations in the two types of space will approach comparability in their respective dimensionalities. The presence of adjoint, $T^{kq}(v) = (-1)^{k-q}T^{k-q}(v)$, and spectral reflection properties [16] in q domains, together with frequency sum rules, mean that the system, in terms of the hamiltonian parameters, is greatly overdetermined, if all the multiquantum q coherences are utilized.

It should be pointed out that as a result of the composite-particle factorization, spin systems decompose into subsystems. For example, $[AX_n]_2$ contains a number of subsystems [39, 40]; the $[AX]_2$ spin subsystem is contained in all odd n $[AX_n]_2$ and the $[AX_2]_2$ subsystem is contained in all even n $[AX_n]_2$. Since such a factorization corresponds to a symmetry reduction within the X_n clusters, further symmetry adaptation of the decomposed $[AX_n]_2$ system is naturally restricted to C_2 projections on the symmetrical component subsystems only. Different total spin systems likewise decompose, but under other forms of the symmetric group, $\mathscr{S}_n$. These spin subsystems are similarly described using the operator basis $T^{kq}(k_Ak_{A'})T^{k'0}(v)$ and $T^{k0}(k_Ak_{A'})T^{k'q'}(v')$ discussed in this paper.

5. Conclusion

Apart from the symmetry factorization under rotational and point group invariance properties, a basis must also be appropriate for calculating the hamiltonian matrix elements. All such matrix elements are readily obtained from the Wigner–Eckart theorems for rotational [41] and point groups [42] which generate selection rules between the tensorial indices. For example the scalar coupling term $\sum_{ij} J_{ij}\,\mathbf{I}_i \cdot \mathbf{I}_j$ cannot change the tensor rank nor mix the total q component. On the other hand it can mix the various v, v' components of the operator basis.

In summary, a procedure for reducing the dimensionality of the Liouville matrix in operator space has been described. This involves first starting with the usual operator basis, $|IM\alpha\rangle\langle I'M'\alpha'|$ which does not lead to any obvious factorization other than $M - M' = q$, and first impose rotational invariance. This results in a multipole operator basis previously discussed [29]. In this work additional permutation symmetries has been imposed on the multipole basis to further factor the Liouville matrix. Finally, the X approximation [15] is used to eliminate various couplings in the weak J limit. Such extensions to the direct method make it possible to obtain the highest degree of factorization of the problem so that subsequent spin dynamic and spectral analyses are more readily treated.

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