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Unitary-group approach to the theory of nuclear magnetic resonance of higher-spin nuclei. III

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The unitary-group approach to the treatment of nuclear-magnetic-resonance spectra of $A_NB_M\cdots$ systems of nuclei with higher-than-$\frac{1}{2}$ spin is presented. The adaptation to permutational and spin symmetries is discussed. Some examples are worked out. The development is made with NMR in mind but is otherwise completely general.

I. INTRODUCTION

In two previous papers,[1,2] hereafter referred to as papers I and II, we presented the unitary-group approach (UGA) to pure spin species, A_N, systems with arbitrary spin. In paper I we demonstrated the techniques for constructing and utilizing permutational symmetry, or S_N, adapted basis states of A_N systems. Paper II clarified various points regarding the construction of S_N adapted basis states using UGA versus more conventional[3] methods and explicitly treated the case of A_3 systems.

In this, the third and concluding paper of this series, we present the unitary-group approach to mixed-spin-species, $A_NB_M\cdots$ systems; that is, where the nuclear spins of species A and B (and so on) are not necessarily the same.

In Sec. II we present the general theory of $A_NB_M\cdots$ systems. In Sec. III we present two methods, utilizing spin-projection operators, by which spin-adapted basis states can be constructed. In Sec. IV an example is given for the case of an A_2B_2 system where the A and B nuclei have spin 1. Finally, in Sec. V we give an example of the treatment of an $A_4B_2C_2$ system.

II. GENERAL THEORY

The permutational-symmetry adapted basis states of an A_N system are labeled $|\sigma^{[\lambda]},(\alpha)_qM\rangle$, where σ denotes the nuclear spin; (α) denotes a Weyl-Young tableau with $SU(2\sigma+1)$-adapted labels α_i $(i=1,2,\ldots,N)$ (the α_i are related to the usual z-projection labels by $\alpha_i=\sigma+1-m_i$); q $(q=1,2,\ldots,Q_M)$ denotes the qth unique arrangement of labels α_i at level M, the sum of m_i's; and $[\lambda]$ denotes an irreducible representation, or partition, of the symmetric group, S_N.

The arrangement of labels α_i in the tableau boxes is in increasing order down the columns and nondecreasing order across the rows. This is referred to as lexical ordering. The complete basis is constructed by considering all possible arrangements of labels $\alpha_i=1,2,\ldots,2\sigma+1$ placed in the tableau boxes in adherence to lexicality conditions. In practice, the generation of the basis states proceeds from a uniquely labeled, highest-M tableau (the set of α_i having minimum values) and subsequent states are generated from this one using the unitary-group single-step generators, $E(\alpha_i+1,\alpha_i)$. The matrix elements of these generators are obtained using Harter's jawbone formula and can be evaluated during the basis generation process. The resulting Q_M by Q_{M-1} ($M=M_{\max}$ to $-M_{\max}+1$) matrices are sparse and always contain elements expressible in the form $\sqrt{a/b}$ (a/b rational).[4]

Examples of tableaux for various irreps of spin-1 and spin-$\frac{3}{2}$ bases are shown in Tables I, II, and III of paper I. The correlations between $SU_{[\lambda]}(2\sigma+1)$ and $R(3)$ are also shown in those tables. Examples of transformation coefficients are given in Eq. (3.3) and Table VI of paper I.

The case of $A_NB_M\cdots$ systems can be treated using direct products of A_N and B_M (and so on) permutational-symmetry adapted basis states. In group theoretical terms, we are seeking the reduction of $SU(2\sigma_1+1)\times SU(2\sigma_2+1)\times\cdots$ into its irreps. Using conventional approaches one would perform the evaluation of multipole operators, etc., within each pure spin-species system and then couple the results explicitly, using a technique similar to that of Siddall,[3] for instance. For computer implementation, however, a different approach is often more practical.

The basis states of an $A_NB_M\cdots$ system are denoted as $|\sigma_1^{[\lambda_1]}\sigma_2^{[\lambda_2]}\cdots;(\alpha)_qM\rangle$, where the labels σ_t and $[\lambda_t]$ $(t=1,2,\ldots,T$, the number of spin species) refer to the spin and S_{N_t} partition labels, respectively, of the tth pure spin species. As in the case of A_N systems, $(\alpha)_q$ refers to the qth arrangement of labels α_i in tableau boxes at level M, where M is the sum of all m_i in all spin species. Assuming that M_t is the sum of m_i labels within the tth pure species and there are Q_{M_t} subtableaux at that level for that species, the label q now ranges over $q=1$ to $\sum_{M_t}\prod_t^T Q_{M_t}$, where the sum over M_t levels is restricted to the set of M_t satisfying $\sum_t^T M_t=M$.

The matrix elements of unit irreducible tensor, or multipole, operators I_q^k, is defined as

$$I_q^k=\sum_{i,j}^{N}(-1)^{\sigma_j-m_j}\begin{pmatrix}\sigma_i' & k & \sigma_j\\ -m_i' & q & m_j\end{pmatrix}E(\alpha_i',\alpha_j)\ ,\qquad N=\sum_t N_t\ .$$

The evaluation of these proceeds in a manner directly related to that for pure spin-species systems. Since no interspecies effects are considered, the operator is expressible in the form

$$I_q^k=\sum_t^T I_q^k(t)$$
$$=\sum_t^T \sum_{i,j}^{N_t}(-1)^{\sigma_t-m_j}\begin{pmatrix}\sigma_t & k & \sigma_t\\ -m_j' & q & m_j\end{pmatrix}E(\alpha_i',\alpha_j)\ ,$$

where the sum over contributions from each pure species is made explicit. In a similar manner, the evaluation of two-particle operators such as $I^k\cdot I^k$ can be simplified by writing

$$I^k\cdot I^k=\sum_t^T I^k(t)\cdot I^k(t)+2\sum_{\substack{t,t'\\ t<t'}}^T I^k(t)\cdot I^k(t')\ ,$$

using the fact that $I_q^k(t)$ and $I_q^k(t')$ commute when $t\neq t'$.

III. TRANSFORMATION TO SPIN-ADAPTED STATES

The tableau basis constitutes permutational-adapted many-spin basis states. In many applications, however, there is a need to compute matrix elements in a basis such that its members are simultaneous eigenstates of S^2 and S_Z, that is, a spin-adapted basis. There are two ways to achieve this. One, by transforming the pure-species tableau basis to states of total spin and the other by transforming the mixed-species tableau basis to states of total resultant spins.

The "highest" tableau formed from the unique product of pure-species highest tableaux forms an eigenstate $|\sigma_1^{[\lambda_1]},\sigma_2^{[\lambda_2]}\ldots,\ I_{\max}M_{\max}\rangle$ of the spin operator S^2, where $\mathbf{S}=\sum_{t=1}^T\mathbf{S}_t$, with eigenvalue $I_{\max}\ (I_{\max}+1)$ where $I_{\max}=M_{\max}$ has the value of the maximum sum M. By operating successively on this state with the lowering operator

$$S_-=\sum_{t=1}^T S_{t-}$$
$$=-\sum_t^T\sum_i^{N_t}\left[\frac{\alpha_i(2\sigma_t+1-\alpha_i)}{2}\right]^{1/2}E(\alpha_i+1,\alpha_i)\ ,$$

one produces states $|\sigma_1^{[\lambda_1]}\sigma_2^{[\lambda_2]}\ldots,I_{\max}M\rangle$, and $M=I_{\max},\ldots,-I_{\max}$. At each new M level there may arise orthogonal states labeled $|\sigma_1^{[\lambda_1]}\sigma_2^{[\lambda_2]}\ldots,\ IM=I\rangle$, $I<I_{\max}$, which must be expressed in terms of linear combinations of tableaux. The number of such states is the difference $\Delta Q_M=Q_M-Q_{M+1}$, $M\geq 0$. Most often it is the case that $\Delta Q_M>1$, hence the need to distinguish between two or more states of the same total spin I.

Pure-species spin-adapted basis states can be constructed as

$$|\sigma_1^{[\lambda_1]}\sigma_2^{[\lambda_2]}\ldots,I_1M_1I_2M_2\cdots I_TM_T\rangle\ .$$

Starting from the highest state

$$|\sigma_1^{[\lambda_1]}\sigma_2^{[\lambda_2]}\ldots,I_{1\max}M_1\rangle=|I_{1\max}\cdots I_{T\max}M_T=I_{T\max}\rangle\ .$$

We first apply lowering operators S_{t-} within each pure species producing states

$$|\sigma_1^{[\lambda_1]}\ldots,\ldots,I_{t\max}M_t=I_{t\max}-1\cdots\rangle$$

or T new states. If additional states exist orthogonal to these maximum spin states, then they must be projected out. One can use a Gram-Schmidt orthogonalization procedure as used by Drake, Drake, and Schlesinger[5] for this purpose. It should be noted that this method is able to resolve cases where more than one state of given spin I is produced.

Alternatively, total resultant spin-adapted basis states are constructed as

$$|\sigma_1^{[\lambda_1]}\cdots\sigma_T^{[\lambda_T]},I_1\cdots I_T,I_{12}I_{123}\cdots I_{12\cdots T}\rangle\ .$$

Once again we start with the highest tableau where $I_t=I_{t\max}$ and the intermediate resultant spins

$$I_{1\cdots t\max}=\sum_{r=1}^t I_{r\max}\ .$$

Application of the lowering operator S_- allows one to produce states of varying M. However, the application of projection operators as above *fails* to resolve states with the correct I_t and $I_{1\ldots t}$ labeling. Instead, *linear combinations* of properly labeled states are obtained.

The projection of the correct spin-adapted states can be achieved by the application of a spin-eigenfunction projection operator, proposed originally by Lowdin,[6] of the form

$$P_I=\prod_{K\neq I}[S^2-K(K+1)]\ .$$

The actual operators used as adapted to each spin label required in the representation and the product is over spins not equal to I. The process in practice has the following simplifying features. The first is that the projection operator is applied successively at each new M level, and so it restricts the range of $K\neq I$ states to those already present at the current M level. The other has to do with the order of application of the pure spin-species projection operators; namely, a general spin-projection operator will be expressed as

$$P_{I_1\cdots I_TT_{12}\cdots I_{1-T}}$$
$$=P_{I_{1\ldots T}}P_{I_{1\ldots T-1}}\cdots P_{I_{12}}P_{I_T}P_{I_{T-1}}\cdots P_{I_1}\ .$$

In general then, we will require matrix elements of the operators S_t^2 and $\mathbf{S}_r\cdot\mathbf{S}_t$ in the tableau basis. These can be efficiently evaluated and stored at the beginning of the projection process and reused as necessary in the application of the general operator above, *and* in other operators.

It should be noted that the operators above do not produce normalized linear combinations, hence the need to compute the normalization factor. As should be expected, it is also possible that application of the P operator to a given tableau may result in a zero projection. This simply means that the tableau chosen does not contribute to the desired spin-adapted state, hence a different tableau must be chosen to operate on.

A word about phase convention is in order. First, matrix elements of the one-body, one-step operators are all set to be positive. Second, for both pure- and mixed-species systems, the projection operators used in the generation of eigenvectors guarantees a definite consistent phase (see Ref. 5). Thus the phase convention used in the UGA is in harmony with the one used in standard vector coupling approaches. This correspondence is achieved by equating the highest tableau state with the highest $R(3)$ state.

IV. APPLICATION TO A_2B_2 SPIN-1 SYSTEMS

In paper I we examined the case of A_2B_2 systems where A and B species are both spin 1. We demonstrated the methods for evaluating multipole operator matrix elements in the tableau basis and the subsequent production of spin-adapted states $|\sigma^{[\lambda]},I,M\rangle$ within each pure-species system. Mixed-species states of the form $|\sigma_1^{[\lambda_1]}\sigma_2^{[\lambda_2]},I_1M_1I_2M_2\rangle$ were produced by taking direct products of pure-species spin-adapted states. However, we were able to produce total resultant spin-adapted states $|\sigma_1^{[\lambda_1]}\sigma_2^{[\lambda_2]},I_1I_2IM\rangle$ only through the use of explicit vector coupling.

We shall demonstrate here the use of the spin-eigenfunction projection-operator technique for producing states of total spin directly from mixed-species tableaux. From Table II of paper I, we obtain the ΔQ_M values for partitions [2][2], $[2][1^2]$ $(=[1^2][2])$, and $[1^2][1^2]$. It should be noted that the tableaux listed in Table II of paper I represent direct products of tableaux and not S_N $(N=N_1+N_2)$ adapted tableaux; that is, the tableau shapes for each pure species are disconnected. Thus a tableau expressed as $\substack{11\\44}$ is really just 11×44. In practice a table like Table II is never produced in its entirety as it requires storage totaling the product of pure-species irrep dimensions. Instead, each pure-species set is stored separately requiring only the sum of those dimensions worthy of storage.

It will be sufficient to consider the [2][2] system. The highest tableau, highest spin state is given as

$$|2244\rangle = |11\rangle\times|44\rangle .$$

For brevity we have used the notation $|I_1I_2IM\rangle$, suppressing the partition labels, and to avoid confusion in the tableau labeling we use labels 1, 2, and 3 to denote species-1 states and 4, 5, and 6 to denote species-2 states.

At level $M=3$ we have $\Delta Q_3=1$, indicating that an $I=3$ state is also present. From the angular momentum addition rule $|I_1-I_2|\le I\le I_1+I_2$, it is evident that since $I_1=I_2=2$, then $I=0,1,\ldots,4$. Hence, the new state at $M=3$ must be the state $|2233\rangle$. Clearly at least one new state of the form $|22IM=I\rangle$ will arise at each M level, $M=0,1,\ldots,4$.

The spin-projection operator which we apply at $M=3$ reduces to

$$P_{223}=(S_1^2+S_2^2+2\mathbf{S}_1\cdot\mathbf{S}_2-20)$$

due to the fact that no pure-species spins other than $I_1=I_1=2$ can exist. (Equivalently, the relevant pure-species spin operators reduce to the identity operators.) Applying the S_1^2, S_2^2, and $2\mathbf{S}_1\cdot\mathbf{S}_2$ operators successively to the first tableau, we find

$$S_1^2|11\rangle|45\rangle=6|11\rangle|45\rangle ,$$

$$S_2^2|11\rangle|45\rangle=6|11\rangle|45\rangle ,$$

$$\begin{aligned}2\mathbf{S}_1\cdot\mathbf{S}_2|11\rangle|45\rangle\\ &=2(\mathbf{S}_{10}\cdot\mathbf{S}_{20}-S_{1-}S_{2+}-S_{1+}S_{2-})|11\rangle|45\rangle\\ &=2(2\cdot 1|11\rangle|45\rangle+\sqrt{2}\cdot\sqrt{2}|12\rangle|44\rangle+0)\\ &=4(|11\rangle|45\rangle+|12\rangle|44\rangle) .\end{aligned}$$

Using these results, we have

$$\begin{aligned}P_{223}|11\rangle|45\rangle&=[(6+6+4)|11\rangle|45\rangle+4|12\rangle|44\rangle\\ &\quad-20|11\rangle|45\rangle]\\ &=-4(|11\rangle|45\rangle-|12\rangle|44\rangle) .\end{aligned}$$

After normalizing, we find

$$|2233\rangle=\sqrt{1/2}|11\rangle|45\rangle-\sqrt{1/2}|11\rangle|45\rangle .$$

As a check we operate on the state $|2244\rangle$ with the lowering operator to obtain

$$\begin{aligned}S_-|2244\rangle&=-\sqrt{4}|2243\rangle\\ &=(S_{1-}+S_{2-})|11\rangle|44\rangle\\ &=(-\sqrt{2}|12\rangle|44\rangle)+(-\sqrt{2}|11\rangle|45\rangle)\\ &=-\sqrt{2}(|12\rangle|44\rangle+|11\rangle|45\rangle) ,\end{aligned}$$

from which follows the result

$$|2243\rangle=\sqrt{1/2}(|11\rangle|45\rangle+|12\rangle|44\rangle) .$$

Obviously this state is orthogonal to the projected state $|2233\rangle$.

At level $M=2$ we find $\Delta Q_3=3$. As before, we must have one state labeled $|2222\rangle$. The remaining two states can only differ in the I_1 or I_2 labels. By choosing $I_1=2$, it must follow that $I_2=0$; similarly, we must also have a state with $I_1=0$ and $I_2=2$. Finally, there will also be $I=3,4$ states present at this level. Thus the projection operators to be used are

$$P_{202}=(S^2-20)(S^2-12)(S_2^2-6)(S_1^2-0)$$

for the state $|2022\rangle$,

$$P_{022}=(S^2-20)(S^2-12)(S_2^2-0)(S_1^2-6)$$

for the state $|0222\rangle$, and

$$P_{222}=(S^2-20)(S^2-12)(S_2^2-0)(S_1^2-0)$$

for the state $|2222\rangle$.

Due to the ordering of the mixed-species tableaux, the best strategy to adopt is to apply the pure-species projection operators with highest I_1 first, then proceed to lower I_1 values. This is because the species-1 tableaux have M_1 sums which are nonincreasing from $q=1$ to Q_M, hence they will contribute to I_1 labeled states starting only from below a certain value. This maximizes the probability of avoiding applications of P operators which result in zeros. Also important from the computational viewpoint is to collect the matrix elements of the S_1^2, S_2^2, and $2\mathbf{S}_1\cdot\mathbf{S}_2$ operators only as they are required and access them for repeated use.

The nonzero matrix elements are

$$\langle 11\times46|S_1^2|11\times46\rangle=\langle 11\times55|S_1^2|11\times55\rangle=\langle 12\times45|S_1^2|12\times45\rangle=6\,,$$

$$\langle 12\times45|S_2^2|12\times45\rangle=\langle 13\times44|S_2^2|13\times44\rangle=\langle 22\times44|S_2^2|22\times44\rangle=6\,,$$

$$\langle 13\times44|S_1^2|13\times44\rangle=\langle 11\times46|S_2^2|11\times46\rangle=2\,,$$

$$\langle 13\times44|S_1^2|22\times44\rangle=\langle 11\times46|S_2^2|11\times55\rangle=2\sqrt{2}\,,$$

$$\langle 22\times44|S_1^2|22\times44\rangle=\langle 22\times55|S_2^2|11\times55\rangle=4\,,$$

$$\langle 11\times46|2\mathbf{S}_1\cdot\mathbf{S}_2|12\times45\rangle=\langle 13\times44|2\mathbf{S}_1\cdot\mathbf{S}_2|12\times45\rangle=2\sqrt{2}\,,$$

$$\langle 11\times55|2\mathbf{S}_1\cdot\mathbf{S}_2|12\times45\rangle=\langle 22\times44|2\mathbf{S}_1\cdot\mathbf{S}_2|12\times45\rangle=4\,,$$

$$\langle 12\times45|2\mathbf{S}_1\cdot\mathbf{S}_2|12\times45\rangle=1\,.$$

Using these values, we apply the operator P_{202} to the first tableau at $M=2$,

$$\begin{aligned}
P_{202}|11\times46\rangle &=(S^2-20)(S^2-12)(S_2^2-6)S_1^2|11\times46\rangle\\
&=6(S^2-20)(S^2-12)(S_2^2-6)|11\times46\rangle\\
&=2\cdot6(S^2-20)(S^2-12)(-2|11\times46\rangle+\sqrt{2}|11\times55\rangle)\\
&=2\cdot6(S^2-20)\{-2[(-12+6+2)|11\times46\rangle+2\sqrt{2}|11\times55\rangle+2\sqrt{2}|12\times45\rangle]\\
&\qquad+\sqrt{2}[(-12+6+4)|11\times55\rangle+2\sqrt{2}|11\times46\rangle+4|12\times45\rangle]\}\\
&=-2\cdot6\cdot6(S^2-20)(-2|11\times46\rangle+2|11\times55\rangle)\\
&=-2\cdot6\cdot6\{-2[(-20+6+2)|11\times46\rangle+2\sqrt{2}|11\times55\rangle+2\sqrt{2}|12\times45\rangle]\\
&\qquad+\sqrt{2}[(-20+6+4)|11\times55\rangle+2\sqrt{2}|11\times46\rangle+4|12\times45\rangle]\}\\
&=-2\cdot6\cdot6\cdot14(2|11\times46\rangle-\sqrt{2}|11\times55\rangle)\,.
\end{aligned}$$

Normalizing this combination yields the results

$$|2022\rangle=\sqrt{2/3}\,|11\times46\rangle-\sqrt{1/3}\,|11\times55\rangle\,.$$

We can easily check this result using standard vector coupling since the $|11\rangle$ species-1 state is an $I=M=2$ state, and we have

$$|2022\rangle=\langle 2200|22\rangle\,|22\rangle\times|00\rangle=|22\rangle\times|00\rangle\,.$$

The $|00\rangle$ state can be computed and is given as

$$|00\rangle=\sqrt{2/3}\,|46\rangle-\sqrt{1/3}\,|55\rangle\,.$$

The remaining spin states are found by applying

$$\begin{aligned}
P_{222}|12\times45\rangle &=(S^2-20)(S^2-12)S_2^2S_1^2|12\times45\rangle\\
&=6\cdot6(S^2-20)(S^2-12)|12\times45\rangle\\
&=6\cdot6(S^2-20)[(-12+6+6+2)|12\times45\rangle+2\sqrt{2}|11\times46\rangle\\
&\qquad+4|11\times55\rangle+2\sqrt{2}|13\times44\rangle+4|22\times44\rangle]\\
&=6\cdot6\{2(2|12\times45\rangle+2\sqrt{2}|11\times46\rangle+4|11\times55\rangle+2\sqrt{2}|13\times44\rangle+4|22\times44\rangle)\\
&\qquad+2\sqrt{2}[(-20+6+2)|11\times46\rangle+2\sqrt{2}|11\times55\rangle+2\sqrt{2}|12\times45\rangle]\\
&\qquad+4[(-20+6+4)|11\times55\rangle+2\sqrt{2}|11\times46\rangle+4|12\times45\rangle]\\
&\qquad+2\sqrt{2}[(-20+2+6)|13\times44\rangle+2\sqrt{2}|22\times44\rangle+2\sqrt{2}|12\times45\rangle]\\
&\qquad+4[(-20+4+6)|22\times44\rangle+2\sqrt{2}|13\times44\rangle+4|12\times45\rangle]\}\\
&=-6\cdot6\cdot12(\sqrt{2}|11\times46\rangle+2|11\times55\rangle-3|12\times45\rangle+\sqrt{2}|13\times44\rangle+2|22\times44\rangle)\,.
\end{aligned}$$

By normalizing we find

$$|2222\rangle=\sqrt{2/21}\,|11\times46\rangle+\sqrt{4/21}\,|11\times55\rangle-\sqrt{9/21}\,|12\times45\rangle+\sqrt{2/21}\,|13\times44\rangle+\sqrt{4/21}\,|22\times44\rangle\,.$$

TABLE I. Tableau basis and $R(3)$ correlation of $(\frac{3}{2})^{[31]}$ system.

M	Tableaux	ΔQ_M	$R(3)$
5	$\begin{array}{l}111\\5\end{array}$	1	5
4	$\begin{array}{l}111\\3\end{array}\ \begin{array}{l}112\\2\end{array}$	1	4
3	$\begin{array}{l}111\\4\end{array}\ \begin{array}{l}112\\3\end{array}\ \begin{array}{l}113\\2\end{array}\ \begin{array}{l}122\\2\end{array}$	2	3,3′
2	$\begin{array}{l}112\\4\end{array}\ \begin{array}{l}114\\2\end{array}\ \begin{array}{l}113\\3\end{array}\ \begin{array}{l}122\\3\end{array}\ \begin{array}{l}123\\2\end{array}$	1	2
1	$\begin{array}{l}113\\4\end{array}\ \begin{array}{l}114\\3\end{array}\ \begin{array}{l}122\\4\end{array}\ \begin{array}{l}124\\2\end{array}\ \begin{array}{l}123\\3\end{array}\ \begin{array}{l}133\\2\end{array}\ \begin{array}{l}222\\3\end{array}$	2	2,2′
0	$\begin{array}{l}114\\4\end{array}\ \begin{array}{l}123\\4\end{array}\ \begin{array}{l}134\\2\end{array}\ \begin{array}{l}124\\3\end{array}\ \begin{array}{l}133\\3\end{array}\ \begin{array}{l}222\\4\end{array}\ \begin{array}{l}223\\3\end{array}$	0	

Finally, using the operator P_{022} we obtain

$$P_{022}\,|\,13\times 44\rangle = -2\cdot 6\cdot 6\cdot 14(2\,|\,13\times 44\rangle = \sqrt{2}\,|\,22\times 44\rangle)$$

or, after normalizing

$$|\,0222\rangle = \sqrt{2/3}\,|\,13\times 44\rangle - \sqrt{1/3}\,|\,22\times 44\rangle \ .$$

This procedure is continued at levels $M=1$ where only a single additional state arises ($\Delta Q_1 = 1$) which must be a $|\,2211\rangle$ state, and $M=0$ where two additional states arise ($\Delta Q_0 = 2$) which must be $|\,2200\rangle$ and $|\,0000\rangle$. All other states may be obtained using the lowering operator.

The use of the spin-eigenfunction projection operators has allowed us to proceed directly from the mixed-species tableau basis to pure-species-resultant—spin-adapted states without the need to rely on vector-coupling considerations. The technique is easily extended, furthermore, to cases of more than two pure species as we shall see in the next section.

V. $A_4B_2C_2$ SYSTEM WITH NONEQUIVALENT SPINS

We shall now consider the case of an $A_4B_2C_2$ system where the spin of A is $\frac{3}{2}$ with pure-species S_4 irreps [4], [31], $[2^2]$, and $[1^4]$ and the spins of B and C are both 1 with irreps as in Sec. III. Our aim here is to demonstrate the use of UGA and the spin-eigenfunction projection-operator techniques for a more complicated case to which the method of Siddall[3] cannot be directly extended. It is characteristic of UGA that there is no significant difference in approach to that of the simpler A_2B_2 spin-1 system considered in Sec. IV.

The mixed-species total spin-adapted states are labeled

$$|\,\sigma_1^{[\lambda_1]}\sigma_2^{[\lambda_2]}\sigma_3^{[\lambda_3]}, I_1 I_2 I_3 I_{12} I_{123} M\rangle \ .$$

Considering the case of irreps $[\lambda_1]=[31]$, $[\lambda_2]=[2]$, and $[\lambda_3]=[1^2]$, we find the tableau basis of $(\frac{3}{2})^{[31]}$ given in Table I, $E(\alpha_i+1,\alpha_i)$ matrix elements in Table II, and spin-adapted states in Table III. Those of $(1)^{[2]}$ and $(1)^{[1^2]}$ were given in Table I of paper I. We shall consider an example from the system irrep $(\frac{3}{2})^{[31]}(1)^{[2]}(1)^{[1^2]}$.

The highest tableau is uniquely spin adapted with $I_1=5$, $I_2=2$, $I_3=1$, $I_{12}=7$, and $I_{123}=8$; hence, suppressing irreps labels

$$|\,52178M=8\rangle = {}^{111}_{2}\times 55\times {}^{8}_{9} \ ,$$

where the labels $\alpha_i = 1,2,3,4$ denote the S_Z-projections of $\sigma_1 = \frac{3}{2}$ and $\alpha_i = 5,6,7$ and 8,9,10 are used for the $\sigma_2 = \sigma_3 = 1$ S_Z projections. At level $M=7$, $\Delta Q_7 = 3$ and there must be states $|\,52177M=7\rangle$ and $|\,52167M=7\rangle$. The values of ΔQ_{M_t} at this level are therefore used. These can be expressed as a triple $(\Delta Q_{M_1},\Delta Q_{M_2},\Delta Q_{M_3})$ where $M_1+M_2+M_3=M$. In this case, we have three such triples (1,1,0), (1,0,1), and (1,1,1). If the triple contains a zero, then no new state arising from a new I_t labeling occurs. The third triple (1,1,1) shows that a new spin-$\frac{3}{2}$ species spin state arises which must be an $I_1=4$ state. (Indeed one expects this within the pure species as can be seen from Table I.) Thus we expect to find the state $|\,42167M=7\rangle$.

In the case of the $M=7$ states to be projected out, we require the operators

$$P_{52177} = (S_{123}^2 - 72)(S_{12}^2 - 42)(S_1^2 - 20) \ ,$$

$$P_{52167} = (S_{123}^2 - 72)(S_{12}^2 - 56)(S_1^2 - 20) \ ,$$

$$P_{42167} = (S_{123}^2 - 72)(S_{12}^2 - 56)(S_1^2 - 30) \ ,$$

where the P_{I_2} and P_{I_3} have been reduced to the identity (only $I_2=2$ and $I_3=1$ states contribute at this level to the labeling) and we introduce the notation

$$\mathbf{S}_{12\cdots t} = \sum_{i=1}^{t} \mathbf{S}_i$$

TABLE II. One-step generator matrix elements of $(\frac{3}{2})^{[31]}$.

$$\begin{array}{l}111\\2\end{array}$$

$$\begin{bmatrix}1\\[6pt] \sqrt{2}\end{bmatrix}\ \begin{array}{l}111\\3\\[6pt]112\\2\end{array}$$

$$\begin{array}{ll}\begin{array}{l}111\\3\end{array} & \begin{array}{l}112\\2\end{array}\end{array}$$

$$\begin{bmatrix}1 & 0\\[6pt] \sqrt{3} & \sqrt{2/3}\\[6pt] 0 & \sqrt{4/3}\\[6pt] 0 & \sqrt{2}\end{bmatrix}\ \begin{array}{l}111\\4\\112\\3\\113\\2\\112\\2\end{array}$$

$$\begin{array}{llll}\begin{array}{l}111\\4\end{array} & \begin{array}{l}112\\3\end{array} & \begin{array}{l}113\\2\end{array} & \begin{array}{l}122\\2\end{array}\end{array}$$

$$\begin{bmatrix}\sqrt{3} & 1 & 0 & 0\\[6pt] 0 & \sqrt{2/3} & \sqrt{4/3} & 0\\[6pt] 0 & \sqrt{4} & 0 & \sqrt{1/3}\\[6pt] 0 & 0 & 1 & \sqrt{8/3}\\[6pt] 0 & 0 & 1 & 0\end{bmatrix}\ \begin{array}{l}112\\4\\113\\3\\122\\3\\123\\2\\114\\2\end{array}$$

TABLE III. $(\frac{3}{2})^{[31]}$ spin-adapted basis vectors.

$$|55\rangle = {}_{2}^{111}$$

$$|54\rangle = \sqrt{1/5}(\sqrt{2}\,{}_{3}^{111} + \sqrt{3}\,{}_{2}^{111})$$

$$|53\rangle = \sqrt{1/9\cdot 5}[\sqrt{3}\,{}_{4}^{111} + (\sqrt{9}+\sqrt{4})\,{}_{3}^{112} + \sqrt{8}\,{}_{2}^{112} + \sqrt{9}\,{}_{2}^{122}]$$
$$= \sqrt{1/45}(\sqrt{3}\,{}_{4}^{111} + \sqrt{25}\,{}_{3}^{112} + \sqrt{8}\,{}_{2}^{113} + \sqrt{9}\,{}_{2}^{122})$$

$$|44\rangle = \sqrt{1/5}(\sqrt{3}\,{}_{3}^{111} - \sqrt{2}\,{}_{2}^{112})$$

$$|43\rangle = \sqrt{1/4\cdot 5}[\sqrt{9/2}\,{}_{4}^{111} + (\sqrt{27/2} - \sqrt{8/3})\,{}_{3}^{112} - \sqrt{16/3}\,{}_{2}^{113} - \sqrt{6}\,{}_{2}^{122}]$$
$$= \sqrt{1/120}(\sqrt{27}\,{}_{4}^{111} + \sqrt{25}\,{}_{3}^{112} - \sqrt{32}\,{}_{2}^{113} - \sqrt{36}\,{}_{2}^{122})$$

$$|33\rangle = \sqrt{1/3672}(\sqrt{2601}\,{}_{4}^{111} - \sqrt{867}\,{}_{3}^{112} + \sqrt{96}\,{}_{2}^{113} + \sqrt{108}\,{}_{2}^{122})$$

$$|3'3\rangle = \sqrt{1/17}(\sqrt{9}\,{}_{2}^{113} - \sqrt{8}\,{}_{2}^{122})$$

to denote the intermediate and final spin couplings used.

These operators are then applied to the tableaux

$$|M=7,1\rangle = |{}_{2}^{111}\times 55 \times {}_{10}^{8}\rangle ,$$
$$|M=7,2\rangle = |{}_{2}^{111}\times 56 \times {}_{9}^{8}\rangle ,$$
$$|M=7,3\rangle = |{}_{3}^{111}\times 55 \times {}_{9}^{8}\rangle ,$$
$$|M=7,4\rangle = |{}_{2}^{112}\times 55 \times {}_{9}^{8}\rangle .$$

For example,

$$P_{52177}\,|{}_{2}^{111}\times 55\times{}_{10}^{8}\rangle$$
$$= -2\cdot 10\cdot 14(\sqrt{49}\,|7,1\rangle - \sqrt{2}\,|7,2\rangle - \sqrt{2}\,|7,3\rangle - \sqrt{3}\,|7,4\rangle) ,$$

giving the normalized state

$$|52177M=7\rangle = \sqrt{1/56}(\sqrt{49}\,|1\rangle - \sqrt{2}\,|2\rangle - \sqrt{2}\,|3\rangle - \sqrt{3}\,|4\rangle) .$$

The remaining states are found by applying P_{52167} to the next tableau $|2\rangle$ and P_{42167} to the tableau $|3\rangle$.

At the next level $\Delta Q_6 = 7$ and we find q indexes, expressed as triples: (1,1,0), $(1,0,0)^3$, (2,1,1). From angular momentum addition rules we predict states $|52176\rangle$, $|52166\rangle$, $|52156\rangle$, $|42166\rangle$, and $|42156\rangle$, leaving two states unresolved. From the triple (2,1,1) we determine that two new $I_1 = 3$ states have arisen, hence the remaining spin states are $|32156\rangle$ and $|3'2156\rangle$. The application of the operator P_{32156} to the tableaux $|{}_{4}^{111}\times 55\times{}_{9}^{8}\rangle$ and $|{}_{3}^{112}\times 55\times{}_{9}^{8}\rangle$ gives identical results; hence a third application of P_{32156} to either the tableau $|{}_{2}^{113}\times 55\times{}_{9}^{8}\rangle$ or $|{}_{2}^{122}\times 55\times{}_{9}^{8}\rangle$ is necessary to resolve the second $I_3 = 3'$ labeling. It should be noted that the same problem occurs for this (and similar cases) using Gram-Schmidt orthogonalization and so no relative loss of computational efficiency occurs due to the choice of projection operator.

VI. CONCLUSION

We have once again[1,2] demonstrated the power and versatility of the unitary-group approach in calculations where other methods, such as those of Siddall, become too cumbersome. Typically, for simple cases UGA is not simpler than other approaches. It is precisely at the complex systems level that its power is evident.

During the course of this work, we pointed out a variety of computational strategies for the benefit of the practitioner. We have in the past[7] implemented UGA on small computer systems and found that a highly modularized programming approach (using machine or assembly language) is most effective.

The method is sufficiently general so that it can handle both pure- and mixed-spin-species systems of arbitrary nuclear spin. Although the work is done with NMR in mind, it also has applications to the magnetic properties of transition-metal ions and thus is widely applicable.

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