Theory of nuclear magnetic resonance of higher-spin nuclei: A_3B, A_4B, and more complex spin-1 and spin-$\frac{3}{2}$ systems

T. H. Siddall III and R. L. Flurry, Jr.
Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148
(Received 4 September 1984)

Procedures are presented for solving eigenvalue-eigenvector problems for A_3B, A_4B, and more complex many-spin systems with spins of 1 and $\frac{3}{2}$. Tables of reduced matrix elements and spin set energies are presented. The problem of the proper choice of sign (or phase) for reduced matrix elements is discussed. The symmetry of such systems is explored.

I. INTRODUCTION

In earlier publications [here labeled papers I (Ref. 1), II (Ref. 2), III (Ref. 3), and IV (Ref. 4)] we described the theoretical, computational, and symmetry aspects of working with an angular-momentum basis applied to problems of chemical and spectroscopic interest. Special interest was directed toward the calculation of the nuclear-magnetic-resonance (NMR) spectra of nuclei with spins greater than $\frac{1}{2}$. However, developments along these lines can also be useful in applications to any problem for which an angular-momentum basis is used. For example, the magnetic properties of clusters of transition-metal ions constitute such a problem.[5,6]

The earlier publications were largely restricted to small problems. For these smaller problems a spin-product basis[2,3] serves well enough and can be employed in a direct, straightforward way. However, for even quite modest problems the spin-product basis leads to some very large computations that are inefficient and computer-time consuming. In paper III it was shown that computations are much more efficient when alternative, many-body basis sets are used; therein the discussion was restricted to A_2B_2 systems.

The present work is extended to computations on homonuclear A_3B, A_4B, and A_3B_3 systems with individual spins of 1 or $\frac{3}{2}$. The material developed here and in earlier publications provides for a ready extension to more complex homonuclear systems with the general label $A_{nA}B_{nB}-G_{nG}$, and also to heteronuclear systems.

This work is organized as follows: In Sec. II we discuss the Hamiltonian; in Sec. III, the basis set; in Sec. IV, the matrix-element "machine"; and in Sec. V, the coupling symmetry; Appendixes A and B conclude the paper. Section IV is composed of a number of subsections. As it turns out, two subsidiary considerations require substantial development, namely the factoring of the secular determinants and the phase (or sign) of the reduced matrix elements. These are discussed in Appendix A and B, respectively.

II. THE HAMILTONIAN

The Hamiltonian employed here is divided into two components in the standard fashion. The first component is the Zeeman term, the interactions of single particles or sets of equivalent particles with the magnetic field. The Zeeman contribution is straightforward and does not play a significant part in the discussion below. Pairwise scalar coupling constitutes the second component of the Hamiltonian and is the important component in the discussion here. It is convenient to divide the coupling into two parts: (1) coupling between particles within a set of equivalent particles, and (2) coupling between sets of equivalent particles. The Hamiltonian is written in unit-tensor-operator notation.

The Hamiltonian can be written as

$$H=-\sum_G \omega(G)\hat{I}^I_0(G)-\sum_G\sum_{k=1}^{2I}\sum_i\sum_{j\,(>i)} T^k_G\hat{I}^k(i)\cdot\hat{I}^k(j)-\sum_{k=1}^{2I}\sum_i\sum_{j\,(>i)} T^k_{GiGj}\hat{I}^k(Gi)\cdot\hat{I}^k(Gj)\,, \tag{1}$$

where the first summation is the Zeeman term, and the quadruple summation accounts for coupling within equivalent sets. The T^k_G are coupling constants *within* a set. The scalar-operator products, $\hat{I}^k(i)\cdot\hat{I}^k(j)$, act on individual spins. The triple summation accounts for coupling *between* sets of equivalent nuclei and the scalar products, $\hat{I}^k(Gi)\cdot\hat{I}^k(Gj)$, act between entire sets. For $A_{nA}B$ systems, B would be regarded as a set, but the quadruple sum would not, of course, apply to the single B spin.

III. THE BASIS SET

The basis employed here for A_3 and A_4 clusters is a many-particle basis, the basis set D of paper III. The general ket is $|[\lambda]_A,I_A,M_A\rangle$. $[\lambda]_A$ is the irreducible representation (irrep) in SU(3) for spin 1 or SU(4) for spin $\frac{3}{2}$, I_A is the irrep in R_3, and M_A is the irrep in R_2. The general ket reflects the symmetry of the group-subgroup chain $\mathrm{SU}(2j+1)\supset R_3\supset R_2$. For spin $\frac{3}{2}$ it has been known for some time that the symplectic group $\mathrm{Sp}(2j+1)$

can profitably be included in the chain of nested groups such as $SU(2j+1) \supset Sp(2j+1) \supset R_3 \supset R_2$.[7-9] As will be seen later, our studies substantiate these early findings and even allocate a role to SU(4) that is enhanced over that given it in the literature. However, we shall most often leave the irrep in Sp(4), σ_A, out of the basis ket description.

For convenience in later discussion we will refer to this basis as the *composite particle basis.* This also is in keeping with past practice.

IV. THE MATRIX-ELEMENT "MACHINE"

The matrix-element "machine" for the Zeeman term is straightforward, as inferred from the literature and from our earlier work. It is not discussed further here. However, there is a necessary preliminary to the discussion of the matrix-element machine for the rest of the Hamiltonian.

The necessary preliminary is that the secular determinants for A_3 and A_4 clusters, spin 1 and spin $\frac{3}{2}$, factor completely into 1×1 determinants. (The details are discussed in Appendix A.) This means that eigenvectors from spin-product calculations can be associated with a given ket, $|[\lambda]_A, I_A, M_A\rangle$, in a unique fashion. The spin-product eigenvectors are symmetry-adapted linear combinations (SALC's) of spin-product functions, each adapted to a composite particle ket.

A. Coupling within a set

The quadruple sum in the Hamiltonian (1), the coupling *within* a set, can be dealt with in a very direct way. For spin 1 it is only necessary to make a calculation on a spin-product basis twice, each time inputting different coupling constants [$T^1(A)$ and $T^2(A)$]. This provides the necessary equations to solve for the coupling energy within a set, for each composite-particle ket, as a function of $T^1(A)$ and $T^2(A)$. The same technique applies to spin $\frac{3}{2}$ except that three spin-product calculations are needed in order to express coupling energies within a set as a function of $T^1(A)$, $T^2(A)$, and $T^3(A)$. This procedure has been followed and the results are given as $E(J,I)$ in Tables I and II. The matrix-element machine for coupling between sets is much more complicated and requires most of the remaining text for discussion.

B. Matrix elements between sets

The central component for the matrix-element machine between sets is the Wigner-Eckart theorem. This can be written, for present purposes, as

$$\langle [\lambda]_A, I_A, M_A; [\lambda]_B, I_B, M_B \,|\, \hat{I}^k_q(A)\hat{I}^k_{-q}(B) \,|\, [\lambda]_A, I'_A, M'_A; [\lambda]_B, I'_B, M'_B \rangle$$
$$= (-1)^{I_A - M'_A} \begin{pmatrix} I_A & k & I'_A \\ -M_A & q & M'_A \end{pmatrix} \langle [\lambda]_A, I_A || \hat{I}^k(A) || [\lambda]_A, I'_A \rangle$$
$$+ (-1)^{I_B - M'_B} \begin{pmatrix} I_B & k & I'_B \\ -M_B & q & M'_B \end{pmatrix} \langle [\lambda]_B, I_B || \hat{I}^k(B) || [\lambda]_B, I'_B \rangle \,. \quad (2)$$

For a complete calculation it would be necessary to sum Eq. (2) over all ranks of coupling k, and also over all sets of equivalent spins. The $3j$ symbols (in large parentheses) can be calculated readily. The only difficulty lies in obtaining the reduced matrix elements (RME's), between the angular brackets containing the double vertical bars.

Of the three ways known to us,[10-12] we have chosen the most direct way as our primary way to calculate the reduced matrix elements. This way is to invert the Wigner-Eckart theorem, as it is applied to one-particle or one-set interactions. We have

$$\langle [\lambda]_A, I_A, M_A \,|\, \hat{I}^k_q(A) \,|\, [\lambda]_A, I'_A, M'_A \rangle = (-1)^{I_A - M_A} \begin{pmatrix} I_A & k & I'_A \\ -M_A & q & M'_A \end{pmatrix} \langle [\lambda]_A, I_A || \hat{I}^k || [\lambda]_A, I'_A \rangle \,,$$

which can be inverted to give

$$\langle [\lambda]_A, I_A || \hat{I}^k(A) || [\lambda]_A, I'_A \rangle = \frac{(-1)^{I_A - M_A} \langle [\lambda]_A, I_A, M_A \,|\, \hat{I}^k_q(A) \,|\, [\lambda]_A, I'_A, M'_A \rangle}{\begin{pmatrix} I_A & k & I'_A \\ -M_A & q & M'_A \end{pmatrix}} \,. \quad (3)$$

The $3j$ symbol is readily obtained, as is the matrix element on the right-hand side of Eq. (3) (since the eigenvectors from spin-product calculations are SALC's for the kets, $[\lambda]_A, I_A, M_A\rangle$). For I_A equal to I'_A, the phase (sign) for the RME is also obtained. Phases of SALC's are arbitrary, but this makes no difference when I_A equals I'_A. The difficulty arises when I_A does not equal I'_A. In that event, Eq. (3), of itself, cannot predict the correct sign for the RME. It is necessary to turn to a phase convention or to some computation of phase that it outside of Eq. (3).

As discussed in Appendix B, we have been able to obtain satisfactory signs for RME's with I_A not equal to I'_A.

TABLE I. Set energies and reduced matrix elements for spin-1 systems. These are the reduced matrix elements as they appear in the lower triangle of the spin-only magnetic Hamiltonian matrix.

A_3 systems

$E(1,3)^{a}=-0.5A_{JJ}(1)^{b}-0.1A_{JJ}(2)^{c}$
$E(2,2)=A_{JJ}(2)/5.0$
$E(2,1)=A_{JJ}(1)/3.0$
$E(1,1)=A_{JJ}(1)/3.0-0.6A_{JJ}(2)$
$E(3,0)=A_{JJ}(1)/2.0+A_{JJ}(2)/2.0$

$\mathcal{M}(1,2,3,1)^{d}=(2.0/5.0)\sqrt{21.0}$
$\mathcal{M}(1,1,3,3)=\sqrt{14.0}$
$\mathcal{M}(1,2,3,3)=(3.0/5.0)\sqrt{14.0}$
$\mathcal{M}(2,1,1,1)=1.0$
$\mathcal{M}(2,2,2,1)=\sqrt{3.0}$
$\mathcal{M}(2,1,2,2)=\sqrt{5.0}$
$\mathcal{M}(1,1,1,1)=1.0$
$\mathcal{M}(1,2,1,1)=1.8$

A_4 systems[e]

$E(1,4)=-A_{JJ}(1)-A_{JJ}(2)/5.0$
$E(1,2)=A_{JJ}(1)/6.0-9.0A_{JJ}(2)/10.0$
$E(1,0)=2.0A_{JJ}(1)/3.0-6.0A_{JJ}(2)/5.0$
$E(2,3)=-A_{JJ}(1)/3.0+A_{JJ}(2)/5.0$
$E(2,2)=A_{JJ}(1)/6.0-A_{JJ}(2)/10.0$
$E(2,1)=A_{JJ}(1)/2.0-3.0A_{JJ}(2)/10.0$
$E(3,2)=A_{JJ}(1)/6.0+3.0A_{JJ}(2)/10.0$
$E(3,0)=2.0A_{JJ}(1)/3.0$
$E(4,1)=A_{JJ}(1)/2.0+A_{JJ}(2)/2.0$

$\mathcal{M}(1,1,2,2)=\sqrt{5.0}$
$\mathcal{M}(1,2,2,2)=\sqrt{121.0/21.0}$
$\mathcal{M}(1,1,4,4)=\sqrt{30.0}$
$\mathcal{M}(1,2,4,4)=\sqrt{66.0/7.0}$
$\mathcal{M}(2,1,1,1)=1.0$
$\mathcal{M}(2,2,1,1)=-1.4$
$\mathcal{M}(2,1,2,2)=\sqrt{5.0}$
$\mathcal{M}(2,2,2,2)=\sqrt{7.0/3.0}$
$\mathcal{M}(2,1,3,3)=\sqrt{14.0}$
$\mathcal{M}(2,2,3,3)=(1.0/5.0)\sqrt{14.0}$
$\mathcal{M}(3,1,2,2)=\sqrt{5.0}$
$\mathcal{M}(3,2,2,2)=-\mathcal{M}(2,2,2,2)$
$\mathcal{M}(4,1,1,1)=1.0$
$\mathcal{M}(4,2,1,1)=1.0$
$\mathcal{M}(2,2,2,1)=-2.0\sqrt{2.0/5.0}$
$\mathcal{M}(2,2,3,2)=-2.0\sqrt{14.0/15.0}$
$\mathcal{M}(2,2,3,1)=-(2.0/5.0)\sqrt{14.0}$
$\mathcal{M}(3,2,2,0)=-2.0\sqrt{1.0/3.0}$
$\mathcal{M}(1,2,4,2)=-6.0\sqrt{6.0/35.0}$
$\mathcal{M}(1,2,2,0)=-2.0\sqrt{14.0/15.0}$

[a]The $E(J,I)$ are the coupling energy within a set of spins in terms of the coupling constants. The first index represents the SU(3) label (1=[3], 2=[2,1], 3=[1^3]). The second index is I_A.
[b]$A_{JJ}(1)$ is the first-rank coupling constant.
[c]$A_{JJ}(2)$ is the second-rank coupling constant.
[d]The $\mathcal{M}(J,R,I,I')$ are the reduced matrix elements. The first index represents the SU(3) label, the second is the rank of coupling, and the third and fourth are I_A and I'_A.
[e]For the four-spin system, the first index is now 1=[4], 2=[3,1], 3=[2^2], and 4=[2,1^2].

Complete RME's for the A_3 and A_4 systems with spin 1 and spin $\frac{3}{2}$ are given in Tables I and II as $\mathcal{M}(J,R,I,I')$. The sign sets for $I\neq I'$ were arbitrarily chosen from collections of satisfactory sets (see Appendix B).

The coupling within a set of equivalent spins for energies and RME's has been tested for use in A_3B and A_4B systems, and also for A_3B_3, by comparing the results that were obtained from these with results from spin-product calculations. Agreement was obtained to within round-off error. Some of the RME's for A_3 were also calculated using Rach's technique, via fractional parentage coefficients.[11] Complete agreement, as to magnitude, was obtained. However, this technique also suffers from phase difficulty, in that the phase is not determined by the calculation but must be established by convention, when I_A does not equal I'_A.

The coupling energies, within a set of equivalent spins, apply to any system $A_{nA}B_{nB}-G_{nG}$ with nG equal to 3 or 4. The procedures described in paper III are satisfactory for nG equal to 2. Overall, these energies can be calculated for any system, homonuclear or heteronuclear, and for all combinations of nG equal to 2, 3, or 4.

The RME's with I_A equal to I'_A in the tables have an equally broad application. The *absolute* values of RME's with I_A not equal to I'_A are as broadly applicable. The discussion in Appendix B leads to the conclusion that the phases we have chosen for the tables also apply in the general situation. However, it is not a practical matter for us to test this conclusion by complete checking against spin-product calculations.

V. COUPLING SYMMETRY AND SOME OF ITS CONSEQUENCES

Tables III and IV reproduce the correlations between SU(3) and SU(4) and their R_3 subgroup.[7] For spin $\frac{3}{2}$, correlation with Sp(4) is also included. The R_3 double group (including integer and half-integer irreps) is actually used. [Strictly speaking, the correlation is with SU(2), but discussion in terms of R_3 is permissible since R_3 is locally isomorphic with SU(2).] These tables will be useful in the discussion below. In that discussion, attention is primarily focused on the symmetry *within* a set of equivalent spins. Our investigation of the symmetry of coupled spins is incomplete in several important respects. The discussion that follows is in the nature of an interim report.

This discussion is organized around the chain of nested groups, $SU(2j+1)\supset R_3\supset R_2$, with the possibility that perhaps other groups should be inserted into the chain. It should be noted that a set of equivalent spins also has permutational symmetry. The head symmetry in the chain is really $SU(2j+1)[\times]S_n$, an inner product of $SU(2j+1)$ and S_n, the symmetric group of degree n (or the group of permutations on n identical objects). Functions that are symmetry-adapted to $SU(2j+1)$ are automatically adapted to S_n. In addition, the irrep labels in S_n serve equally well as irrep labels in $SU(2j+1)$. For these reasons there is little need to refer explicitly to S_n for most of the discussion. However, one special aspect of S_n which is very important is discussed in the next paragraph.

TABLE II. Set energies and reduced matrix elements for spin-$\frac{3}{2}$ systems. These are the reduced matrix elements as they appear in the lower triangle of the spin-only magnetic Hamiltonian matrix. The indexes are the same as in Table I, except that the I_A are in units of $\frac{1}{2}$ (i.e., 9 represents an I_A of 9/2).

A_3 systems

$E(1,9)=(-9.0/20.0)A_{JJ}(1)-(3.0/20.0)A_{JJ}(2)$
$\quad -(3.0/140.0)A_{JJ}(3)$[a]
$E(2,7)=(-3.0/20.0)A_{JJ}(1)+3.0A_{JJ}(2)/20.0$
$\quad +9.0A_{JJ}(3)/140.0$
$E(1,5)=A_{JJ}(1)/12.0-3.0A_{JJ}(2)/20.0-A_{JJ}(3)/4.0$
$E(2,5)=A_{JJ}(1)/12.0+3.0A_{JJ}(2)/20.0-A_{JJ}(3)/28.0$
$E(2,3)=A_{JJ}(1)/4.0-(7.0/20.0)A_{JJ}(2)+A_{JJ}(3)/4.0$
$E(3,3)=A_{JJ}(1)/4.0+A_{JJ}(2)/4.0+A_{JJ}(3)/4.0$
$E(1,3)=A_{JJ}(1)/4.0-(3.0/20.0)A_{JJ}(2)-(9.0/28.0)A_{JJ}(3)$
$E(2,1)=7.0A_{JJ}(1)/20.0+3.0A_{JJ}(2)/20.0\ -(3.0/20.0)A_{JJ}(3)$

$\mathcal{M}(1,1,9,9)=\sqrt{33.0/2.0}$
$\mathcal{M}(1,2,9,9)=0.5\sqrt{33.0}$
$\mathcal{M}(1,3,9,9)=\sqrt{429.0/196.0}$
$\mathcal{M}(1,2,9,5)=1.5$
$\mathcal{M}(1,3,9,5)=1.5\sqrt{11.0/7.0}$
$\mathcal{M}(1,3,9,3)=6.0\sqrt{3.0/7.0}$
$\mathcal{M}(2,1,7,7)=\sqrt{42.0/5.0}$
$\mathcal{M}(2,2,7,7)=\sqrt{6.0/7.0}$
$\mathcal{M}(2,3,7,7)=-\sqrt{66.0/245.0}$
$\mathcal{M}(2,2,7,5)=12.0\sqrt{1.0/7.0/5.0}$
$\mathcal{M}(2,3,7,5)=\sqrt{5.0(6.0/7.0)}$
$\mathcal{M}(2,2,7,3)=4.0\sqrt{3.0/5.0}$
$\mathcal{M}(2,3,7,1)=6.0\sqrt{1.0/35.0}$
$\mathcal{M}(1,1,5,5)=\sqrt{7.0/2.0}$
$\mathcal{M}(1,2,5,5)=\sqrt{21.0/10.0}$
$\mathcal{M}(1,3,5,5)=1.5$
$\mathcal{M}(1,2,5,3)=4.0\sqrt{6.0/5.0}$
$\mathcal{M}(1,3,5,3)=2.0\sqrt{3.0/7.0}$
$\mathcal{M}(2,1,5,5)=\sqrt{7.0/2.0}$
$\mathcal{M}(2,2,5,5)=-\sqrt{3.0/175.0}$
$\mathcal{M}(2,3,5,5)=-3.0/7.0$
$\mathcal{M}(2,2,5,3)=1.2$
$\mathcal{M}(2,2,5,1)=\sqrt{42.0/10.0}$
$\mathcal{M}(2,3,5,1)=\sqrt{15.0/14.0}$
$\mathcal{M}(1,1,3,3)=1.0$
$\mathcal{M}(1,2,3,3)=0.6$
$\mathcal{M}(1,3,3,3)=-9.0/7.0$
$\mathcal{M}(3,1,3,3)=1.0$
$\mathcal{M}(3,2,3,3)=-1.0$
$\mathcal{M}(3,3,3,3)=1.0$
$\mathcal{M}(2,1,3,3)=1.0$
$\mathcal{M}(2,2,3,3)=1.4$
$\mathcal{M}(2,3,3,3)=1.0$
$\mathcal{M}(2,2,3,1)=2.0\sqrt{3.0/5.0}$
$\mathcal{M}(2,1,1,1)=\sqrt{1.0/10.0}$

A_4 systems

$E(1,6)=-0.9A_{JJ}(1)-0.3A_{JJ}(2)-(3.0/70.0)A_{JJ}(3)$
$E(1,4)=-(1.0/6.0)A_{JJ}(1)-0.3A_{JJ}(2)$
$\quad -(5.0/14.0)A_{JJ}(3)$
$E(1,3)=0.1A_{JJ}(1)-0.3A_{JJ}(2)-(33.0/70.0)A_{JJ}(3)$
$E(1,2)=0.3A_{JJ}(1)-0.3A_{JJ}(2)-(39.0/70.0)A_{JJ}(3)$
$E(1,0)=0.5A_{JJ}(1)-0.3A_{JJ}(2)-(9.0/14.0)A_{JJ}(3)$
$E(2,7)=-0.5A_{JJ}(1)+0.1A_{JJ}(2)+(1.0/14.0)A_{JJ}(3)$
$E(2,6)=-(1.0/6.0)A_{JJ}(1)+0.1A_{JJ}(2)\ -(1.0/14.0)A_{JJ}(3)$
$E(2,5)=0.1A_{JJ}(1)-0.5A_{JJ}(2)+(17.0/70.0)A_{JJ}(3)$
$E(2,4)=0.1A_{JJ}(1)+0.3A_{JJ}(2)+(17.0/70.0)A_{JJ}(3)$
$E(2,3)=0.3A_{JJ}(1)+0.1A_{JJ}(2)-(19.0/70.0)A_{JJ}(3)$
$E(2,2)=(13.0/30.0)A_{JJ}(1)-0.5A_{JJ}(2)+0.1A_{JJ}(3)$
$E(2,1)=(13.0/30.0)A_{JJ}(1)+0.1A_{JJ}(2)\ -(23.0/70.0)A_{JJ}(3)$
$E(3,4)=-(1.0/6.0)A_{JJ}(1)+0.3A_{JJ}(2)\ +(1.0/14.0)A_{JJ}(3)$
$E(3,3)=0.3A_{JJ}(1)+0.3A_{JJ}(2)-(9.0/70.0)A_{JJ}(3)$
$E(3,2)=0.3A_{JJ}(1)-0.3A_{JJ}(2)+0.3A_{JJ}(3)$
$E(3,1)=0.5A_{JJ}(1)-0.7A_{JJ}(2)+0.5A_{JJ}(3)$
$E(4,3)=0.1A_{JJ}(1)+0.3A_{JJ}(2)+(17.0/70.0)A_{JJ}(3)$
$E(4,2)=0.3A_{JJ}(1)+0.1A_{JJ}(2)+0.3A_{JJ}(3)$
$E(4,1)=(13.0/30.0)A_{JJ}(1)+0.3A_{JJ}(2)+0.1A_{JJ}(3)$
$E(5,0)=0.5A_{JJ}(1)+0.5A_{JJ}(2)+0.5A_{JJ}(3)$

$\mathcal{M}(1,1,6,6)=\sqrt{182.0/5.0}$
$\mathcal{M}(1,2,6,6)=\sqrt{182.0/11.0}$
$\mathcal{M}(1,3,6,6)=\sqrt{13.0/55.0/4.0}$
$\mathcal{M}(1,1,4,4)=2.0\sqrt{3.0}$
$\mathcal{M}(1,2,4,4)=\sqrt{1.0/77.0(27.0/2.0)}$
$\mathcal{M}(1,3,4,4)=\sqrt{2354.0/533.0}$
$\mathcal{M}(1,1,3,3)=\sqrt{35.0(2.0/5.0)}$
$\mathcal{M}(1,2,3,3)=\sqrt{21.0/2.0}$
$\mathcal{M}(1,3,3,3)=\sqrt{30.0/10.0}$
$\mathcal{M}(1,1,2,2)=\sqrt{2.0}$
$\mathcal{M}(1,2,2,2)=-3.0\sqrt{2.0/7.0}$
$\mathcal{M}(1,3,2,2)=-\sqrt{2.0(2.0/7.0)}$
$\mathcal{M}(1,2,6,4)=3.0\sqrt{26.0/55.0}$
$\mathcal{M}(1,3,6,4)=\sqrt{117.0/22.0}$
$\mathcal{M}(1,3,6,3)=3.0\sqrt{39.0/70.0}$
$\mathcal{M}(1,2,4,3)=-3.0\sqrt{11.0/20.0}$
$\mathcal{M}(1,3,4,3)=-3.0\sqrt{1.0/14.0}$
$\mathcal{M}(1,2,4,2)=3.0\sqrt{11.0/35.0}$
$\mathcal{M}(1,3,4,2)=3.0\sqrt{55.0/98.0}$
$\mathcal{M}(1,2,3,2)=1.0$
$\mathcal{M}(1,3,3,2)=5.0\sqrt{3.0/14.0}$
$\mathcal{M}(1,3,3,0)=4.0\sqrt{1.0/7.0}$
$\mathcal{M}(1,2,2,0)=\sqrt{10.0(2.0/5.0)}$
$\mathcal{M}(2,1,7,7)=\sqrt{22.0}$
$\mathcal{M}(2,2,7,7)=\sqrt{286.0/75.0}$
$\mathcal{M}(2,3,7,7)=0.0$
$\mathcal{M}(2,1,6,6)=2.0\sqrt{3.0}$
$\mathcal{M}(2,2,6,6)=\sqrt{11.0/7.0(9.0/10.0)}$
$\mathcal{M}(2,3,6,6)=3.0\sqrt{11.0/98.0}$
$\mathcal{M}(2,1,5,5)=\sqrt{35.0(2.0/5.0)}$
$\mathcal{M}(2,2,5,5)=\sqrt{7.0/3.0(8.0/5.0)}$
$\mathcal{M}(2,3,5,5)=\sqrt{30.0/5.0}$
$\mathcal{M}(2,1,4,4)=\sqrt{35.0(2.0/5.0)}$
$\mathcal{M}(2,2,4,4)=-\sqrt{7.0/3.0/2.0}$
$\mathcal{M}(2,3,4,4)=-\sqrt{30.0(3.0/10.0)}$
$\mathcal{M}(2,1,3,3)=\sqrt{2.0}$
$\mathcal{M}(2,2,3,3)=2.0\sqrt{2.0/7.0}$
$\mathcal{M}(2,3,3,3)=\sqrt{2.0(3.0/7.0)}$
$\mathcal{M}(2,1,2,2)=2.0\sqrt{1.0/10.0}$
$\mathcal{M}(2,2,2,2)=-\sqrt{2.0/3.0(8.0/5.0)}$
$\mathcal{M}(2,1,1,1)=2.0\sqrt{1.0/10.0}$
$\mathcal{M}(2,2,1,1)=\sqrt{2.0/3.0}$
$\mathcal{M}(2,2,7,6)=\sqrt{33.0/5.0}$

TABLE II. (*Continued.*)

$\mathcal{M}(2,3,7,6)=\sqrt{429.0/98.0}$
$\mathcal{M}(2,2,7,5)=-2.0\sqrt{11.0/15.0}$
$\mathcal{M}(2,3,7,5)=0.0$
$\mathcal{M}(2,2,7,4)=\sqrt{11.0/15.0}$
$\mathcal{M}(2,3,7,4)=3.0\sqrt{11.0/42.0}$
$\mathcal{M}(2,3,7,3)=-\sqrt{33.0}(2.0/7.0)$
$\mathcal{M}(2,2,6,5)=-\sqrt{15.0}(2.0/5.0)$
$\mathcal{M}(2,3,6,5)=0.0$
$\mathcal{M}(2,2,6,4)=-\sqrt{15.0}(3.0/10.0)$
$\mathcal{M}(2,3,6,4)=-3.0\sqrt{11.0/42.0}$
$\mathcal{M}(2,2,6,3)=-\sqrt{6.0/7.0}$
$\mathcal{M}(2,3,6,3)=\sqrt{3.0/7.0}$
$\mathcal{M}(2,3,6,2)=0.0$
$\mathcal{M}(2,3,6,1)=-9.0\sqrt{3.0/98.0}$
$\mathcal{M}(2,2,5,4)=\sqrt{7.0/3.0}(2.0/5.0)$
$\mathcal{M}(2,3,5,4)=0.0$
$\mathcal{M}(2,2,5,3)=-\sqrt{10.0/5.0}$
$\mathcal{M}(2,3,5,3)=0.0$
$\mathcal{M}(2,2,5,2)=\sqrt{7.0/3.0}(4.0/5.0)$
$\mathcal{M}(2,3,5,2)=\sqrt{15.0}(2.0/5.0)$
$\mathcal{M}(2,2,5,1)=\sqrt{2.0/3.0}(4.0/5.0)$
$\mathcal{M}(2,3,5,1)=0.0$
$\mathcal{M}(2,2,4,3)=\sqrt{10.0/5.0}$
$\mathcal{M}(2,3,4,3)=-\sqrt{15.0/7.0}$
$\mathcal{M}(2,2,4,2)=-\sqrt{7.0/3.0}(4.0/5.0)$
$\mathcal{M}(2,3,4,2)=0.0$
$\mathcal{M}(2,2,4,1)=\sqrt{2.0/3.0}$
$\mathcal{M}(2,3,4,1)=\sqrt{3.0/70.0}$
$\mathcal{M}(2,2,3,2)=\sqrt{14.0/15.0}$
$\mathcal{M}(2,3,3,2)=0.0$
$\mathcal{M}(2,2,3,1)=2.0\sqrt{1.0/15.0}$
$\mathcal{M}(2,3,3,1)=\sqrt{30.0}(2.0/7.0)$
$\mathcal{M}(2,2,2,1)=\sqrt{7.0/3.0}(2.0/5.0)$
$\mathcal{M}(3,1,4,4)=2.0\sqrt{3.0}$
$\mathcal{M}(3,2,4,4)=0.0$
$\mathcal{M}(3,3,4,4)=-\sqrt{22.0}(3.0/7.0)$
$\mathcal{M}(3,1,3,3)=\sqrt{2.0}$
$\mathcal{M}(3,2,3,3)=0.0$
$\mathcal{M}(3,3,3,3)=\sqrt{2.0}(8.0/7.0)$
$\mathcal{M}(3,1,2,2)=\sqrt{2.0}$
$\mathcal{M}(3,2,2,2)=0.0$
$\mathcal{M}(3,3,2,2)=-\sqrt{2.0}$
$\mathcal{M}(3,2,4,3)=0.0$
$\mathcal{M}(3,3,4,3)=\sqrt{5.0}(6.0/7.0)$
$\mathcal{M}(3,2,4,2)=\sqrt{10.0}(3.0/5.0)$
$\mathcal{M}(3,3,4,2)=0.0$
$\mathcal{M}(3,2,3,2)=-\sqrt{2.0}$
$\mathcal{M}(3,2,3,1)=0.0$
$\mathcal{M}(3,2,2,1)=\sqrt{15.0}(2.0/5.0)$
$\mathcal{M}(4,1,3,3)=\sqrt{35.0}(2.0/5.0)$
$\mathcal{M}(4,2,3,3)=0.0$
$\mathcal{M}(4,3,3,3)=\sqrt{30.0}/5.0$
$\mathcal{M}(4,1,2,2)=\sqrt{2.0}$
$\mathcal{M}(4,2,2,2)=0.0$
$\mathcal{M}(4,3,2,2)=-\sqrt{2.0}$
$\mathcal{M}(4,1,1,1)=2.0\sqrt{1.0/10.0}$
$\mathcal{M}(4,2,1,1)=0.0$
$\mathcal{M}(4,2,3,2)=\sqrt{70.0}/5.0$
$\mathcal{M}(4,3,3,1)=\sqrt{15.0}(2.0/5.0)$
$\mathcal{M}(4,2,2,1)=\sqrt{30.0}/5.0$

[a] $A_{JJ}(3)$ is the third-rank coupling constant.

Since the basis here is *spin* angular momentum, standing alone, and not a combination of orbital *and* spin angular momentum, the Pauli principle does not apply, in the usual sense. The permutation symmetry of state functions is *not* constrained to the $[1^n]$ irrep, the antisymmetric irrep in S_n. Rather, all irreps of S_n, and also of SU($2j+1$), that have $2j+1$ or fewer rows in their label (Young diagram), are appropriate. This considerably broadens the range of the symmetry as well as that of the computations.

For spin $\frac{3}{2}$, our investigations show that the symplectic group Sp($2j+1$) plays a role and should be inserted into

TABLE III. Correlation table for spin-1 sets.

Number of particles in set	Irrep in SU(3)	Irrep in $R_3(I)$
2	[2]	0, 2
	$[1^2]$	1
3	[3]	1, 3
	[21]	1, 2
	$[1^3]$	0
4	[4]	0, 2, 4
	[31]	1, 2, 3
	$[2^2]$	0, 2
	$[21^2]$	1

TABLE IV. Correlation table for spin-$\frac{3}{2}$ sets.

Number of particles in set	Irrep in SU(4)	Irrep in Sp(4)	Irrep in $R_3(I)$
3	[3]	⟨30⟩	$\frac{3}{2}$, $\frac{5}{2}$, $\frac{9}{2}$
	[21]	⟨10⟩	$\frac{3}{2}$
		⟨21⟩	$\frac{1}{2}$, $\frac{5}{2}$, $\frac{7}{2}$
	$[1^3]$	⟨10⟩	$\frac{3}{2}$
4	[4]	⟨40⟩	0, 2, 3, 4, 6
	[31]	⟨20⟩	1, 3
		⟨31⟩	1, 2, 3, 4, 5
	$[2^2]$	⟨00⟩	0
		⟨11⟩	2
		⟨22⟩	2, 4
	$[21^2]$	⟨11⟩	2
		⟨20⟩	1, 3
	$[1^4]$	⟨00⟩	0

the chain of nested groups to give SU(4)⊃Sp(4) ⊃R_3⊃R_2. Direct evidence for the need to include Sp(4) is found in the complete factoring for A_4, spin $\frac{3}{2}$, into 1×1 determinants. Table IV shows that the ket labels $|[31],I_1,M_A\rangle$, $|[31],I_3,M_A\rangle$, and $|[2^2],I_2,M_A\rangle$ each occur twice. If these kets contained irreps from the complete chain of groups, then, out of necessity, we would be dealing with three 2×2 determinants and not with six 1×1 determinants. There would be coupling matrix elements between kets with the same label, but when Sp(4) is included the kets become unique with no repetition. It appears that basis kets that belong to different irreps in Sp(4) are not connected by coupling. Sp(4) should be included in the chain.

Preliminary investigations on five- and six-spin sets suggests that Sp(4) plays the same role in larger sets. There are also some unexpected zeros in the determinants for spin-$\frac{5}{2}$ systems, but the inclusion of Sp(6) in the chain of groups does not take care of the additional factoring, as does Sp(4) for spin $\frac{3}{2}$. These investigations have not revealed any additional symmetry for integer spin. It might be expected that $R(2j+1)$ would play a role analogous to Sp$(2j+1)$,[7] but this does not seem to be the case. These studies are being continued.

It should be pointed out that it is well known that if only *odd*-rank tensor operators are included in the Hamiltonian, then the secular determinant should factor according to irreps in Sp$(2j+1)$.[13] Odd-rank tensor operators are members of the algebra of Sp$(2j+1)$. However, *even*-rank tensor operators are not members of this algebra and should connect different irreps in Sp$(2j+1)$. Since the Hamiltonian of Eq. (1) contains second-rank operators, it is not obvious why Sp(4) should help factor spin-$\frac{3}{2}$ problems.

For both spin 1 and spin $\frac{3}{2}$ there are no first-rank matrix elements between kets, even for one-particle interactions (not just for coupling, a two-body interaction). In particular, this means that there can be no dipole-induced transitions between states with different I_A values or states that belong to different irreps in SU$(2j+1)$. For spin $\frac{3}{2}$ this also holds for different irreps in Sp(4), the σ_A.

It follows that spectra for two, three, and four spin-1 and spin-$\frac{3}{2}$ systems will be split up into subspectra, or blocks. The subspectra for spin-1 systems will carry $[\lambda]_G$ and I_G labels as well as F_z (the irrep in R_2). For spin-3/2 systems the subspectra will also carry σ_G labels. These arguments apply to all systems, $A_{nA}B_{nB}-G_{nG}$.

ACKNOWLEDGMENTS

We are deeply indebted to Dr. J. L. Sullivan of the University of New Orleans Physics Department. His patient tutoring on various group-theoretical propositions was essential to the progress of the work.

APPENDIX A: FACTORING BY COMPUTER

The procedure for detecting the factoring into 1×1 determinants is as follows: Perform a computation with only the coupling operators of the Hamiltonian (set the Zeeman parameters, the chemical shifts, equal to zero). Repeat the calculation, but with a different set of coupling-constant values as input. If the coefficients of a given eigenvector are invariant (up to a sign change, a phase factor), then the eigenvector is from a 1×1 determinant.

The problem of associating a given eigenvector and the reduced matrix elements with given $|[\lambda]_A,I_A,M_A\rangle$ labels still remains. This is done by working very closely with the relevant correlation table (see Tables III and IV). The M_A value comes directly from the computer output. A comparison of degeneracies seen in the computer output with degeneracies predicted from these tables is one clue to assigning the other quantum numbers in the label. Another clue is found in the fact that the brackets are diagonal in $[\lambda]_A$ and σ_A. Brackets with different I_A values in the bra and ket vanish unless $[\lambda]_A$ and σ_A are the same in both the bra and the ket. Therefore, if two I_A values are connected by off-diagonal matrix elements, they must belong to a given $[\lambda]_A$ and σ_A.

In practice, it is tedious to examine the coefficient matrix of the eigenvectors in detail for invariance. Instead, it is easier to examine the apparent reduced matrix elements for invariance. If the eigenvector is invariant to input, then so will the apparent reduced matrix element that is calculated from it. Invariant apparent reduced matrix elements imply invariant eigenvectors, and, hence, 1×1 determinants. It is seen, then, that the calculation of reduced matrix elements and the detection of factoring into 1×1 determinants are intertwined. The factoring into 1×1 determinants also is directly connected to the determination of the symmetry of the system.

It is also possible, by an extension of these methods, to find the submatrix structure of a matrix when the submatrices are 2×2, $3\times3,\ldots,m\times m$ determinants. For 2×2 determinants and higher submatrices the individual coefficients in the eigenvector are no longer invariant to the coupling-parameter values that are input into the calculations. However, within the eigenvector matrix, the coefficient submatrix corresponding to a given set of quantum labels has the sum of the squares of the coefficients in each column as invariants. We have not needed to utilize this fact in the present investigation, but computer programs to do so can easily be written.

These procedures open the way for a general approach to computer-assisted investigation of symmetry. If a problem can be programmed on some straightforward basis, such as the spin-product basis, then the factoring and degeneracies of the problem can be read from the computer output. In turn, the factoring and degeneracies of the problem provide vital clues as to the symmetry of the problem. In turn, the symmetry of the problem points the way to more efficient basis sets and calculations.

APPENDIX B: SIGNS OF REDUCED MATRIX ELEMENTS

The signs (or phases) of off-diagonal reduced matrix elements ($I_A\neq I'_A$) are not provided by the calculations described in the main text. The difficulty lies in the fact that the phase is not known for the eigenvectors used in the calculation. Spin-product calculations provide the

correct magnitude for the eigenvectors, but the phase is random and arbitrary. This follows from the fact that if ψ is a satisfactory solution to an eigenvalue-eigenvector problem, then $-\psi$ serves equally well. The phase problem occurs, however, only for off-diagonal reduced matrix elements. The phase of diagonal RME's ($I_A = I'_A$) is independent of the phase of the eigenvector.

The phase problem was initially solved here by an inelegant expedient. This involved looping calculations made on a composite basis for A_3B and A_4B systems over permutations of the signs of the off-diagonal RME's. A set of signs was accepted as being correct when the eigenvalues obtained in that loop agreed with the eigenvalues obtained with a spin-product basis.

While this process provides satisfactory phases for the specific systems, A_3B and A_4B, it has serious shortcomings. First, there is no assurance that the phases obtained in this manner will serve for other cases. The absolute values of the RME's are correct for the system $A_{nA}B_{nB}-G_{nG}$, but the question of phase is not answered for the general case. Second, it is not a practical matter to apply an unguided looping technique to individual systems in all possible combinations. For one thing, the calculations become too large. Third, such a brute-force process lacks esthetic appeal. In order to at least mitigate these difficulties, we are attempting to develop a mathematics for the phase of RME's.

The underpinning for this mathematics is the fact that the eigenvalues of a characteristic determinant do not change if the signs of matrix elements are changed for an entire row and the corresponding column. This leaves the diagonal matrix element unaffected, but changes the sign for all off-diagonal matrix elements in the row and column. The development is best continued by working with an example. The chosen example is A_3B, spin $\frac{3}{2}$, $[21]_A$ irrep, with F_z equal to -2.

Table V represents the lower triangle of the matrix of *reduced* matrix elements for this situation. Whatever sign changes that are made in this matrix will be reflected in the complete secular matrix. Each entry is designated by two numbers. The numbers stand for I_A and I'_A, in units of $\frac{1}{2}$. For example, 13 signifies that I_A equals $\frac{1}{2}$, and I'_A, $\frac{3}{2}$. It is not necessary to state the rank of RME's. The *relative* signs for different-rank RME's are fixed for a given I_A and I'_A. This follows, since whatever the phases for eigenvectors may be, the same eigenvectors with the same sign are used in calculating RME's for a given I_A and I'_A, irrespective of rank.

It is very important to note that diagonal RME's ($I_A = I'_A$) do occur *off the diagonal* at certain positions ($A_{7,10}$, $A_{8,10}$, $A_{9,10}$, $A_{3,2}$, $A_{6,4}$, $A_{6,5}$, $A_{8,7}$, $A_{9,7}$, and $A_{9,8}$). The signs of diagonal RME's ($I_A = I'_A$) are fixed and must not be changed. The freedom to change sign is restricted to off-diagonal RME's ($I_A \neq I'_A$). If, for example, the signs for the second row (column) are changed, then they must also be changed for the third row (column). In this fashion, $A_{3,2}$ has its sign changed, but then it is changed back again to its original value. In a similar manner, rows 4, 5, and 6 must all be changed together if any is changed. Likewise, rows 7, 8, 9, and 10 must be changed together. Finally, there is freedom to change in combinations of the fundamental changes: (1); (2,3); (4,5,6); (7,8,9,10). These produce a total of seven sign changes, starting from a given set. [Note that there are redundancies. The combination (1); (2,3); (4,5,6) produces the same result as (7,8,9,10).] Including the starting set, this gives a total of eight sets based on that set.

If any one correct set of signs (for $I_A \neq I'_A$) is known, then the seven other correct sign sets can be obtained. The total set of correct sets is given in Table VI. It should be noted that there is a possible total of 64 sets of six signs each. These 64 are divided into eight sets of sets. Given one set from any of these sets of sets, the remaining seven sets are readily generated by the sign-change operators. However, only one of the eight sets of sets gives correct eigenvalues and this set of sets is given in Table VI. The identical set of sets was generated by the looping technique.

The fundamental sign-change operators provide the generators of a group. There are four fundamental sign-change operators, but any one of them is redundant. It follows that these operators generate a group that is isomorphic to $S_2 \otimes S_2 \otimes S_2$, where S_2 is the symmetric group of degree 2. This group is isomorphic to the point group D_{2h}.

These studies were extended to other situations that occur for A_3B and A_4B spin-1 and spin-$\frac{3}{2}$ systems. The same sort of results were obtained. These considerations

TABLE V. Occurrence of reduced matrix elements in the matrix for A_3B, spin $\frac{3}{2}$. Only the spin labels for the lower triangle are listed. A given entry in the matrix gives the spin labels, in units of $\frac{1}{2}$. For example, the 15 in the A_{41} position signifies that the reduced matrix element is $\langle [21], \frac{1}{2} | \hat{T}^k | [21], \frac{5}{2} \rangle$. $[\lambda]_A = [21]$, $F_z = -2$.

11									
13	33								
13	33	33							
15	35	35	55						
15	35	35	55	55					
15	35	35	55	55	55				
17	37	37	57	57	57	77			
17	37	37	57	57	57	77	77		
17	37	37	57	57	57	77	77	77	
17	37	37	57	57	57	77	77	77	77

TABLE VI. Correct sign sets for reduced matrix elements ($I_A \neq I'_A$ for A_3B spin $\frac{3}{2}$, [21], $F_z=-2$. Note that $\langle [\lambda]_A, I'_A||\hat{I}^k||[\lambda]_A, I_A\rangle = (-1)^k\langle [\lambda]_A, I_A||\hat{I}^k||[\lambda]_A, I'_A\rangle$. There are eight signs in a set. However, there are only six independent signs. Relative signs for different ranks of the otherwise same RME are fixed. Some RME's are not represented in the table. The missing RME's all have zero value.

Rank, I_A, I'_A							
2, $\frac{5}{2}, \frac{7}{2}$	3, $\frac{5}{2}, \frac{7}{2}$	2, $\frac{3}{2}, \frac{7}{2}$	3, $\frac{1}{2}, \frac{7}{2}$	2, $\frac{3}{2}, \frac{5}{2}$	2, $\frac{1}{2}, \frac{5}{2}$	3, $\frac{1}{2}, \frac{5}{2}$	2, $\frac{1}{2}, \frac{3}{2}$
−	+	−	+	−	+	−	+
−	+	−	+	+	+	−	+
−	+	−	−	−	−	+	−
−	+	−	−	+	−	+	−
+	−	+	+	−	−	+	−
+	−	+	+	+	−	+	−
+	−	+	−	−	+	−	+
+	−	+	−	+	+	−	+

can also be extended to the general $A_{nA}B_{nB}-G_{nG}$ situation.

It follows that since sign sets for each set of equivalent nuclei occupy separate spaces (in the sense of linear algebra), the spaces are independent of each other. The overall group of the sign changes for the general system is just group $A\times$group B—group G. The correct set of sets is just the product of the correct set of sets over the individual sets of equivalent nuclei.

This finding was tested by computations on an A_3B_3, spin-$\frac{3}{2}$ system with $[\lambda]_A=[\lambda]_B=[21]$, $F_z=-5$, $F_{zA}=F_{zB}=-\frac{5}{2}$. All 64 sign sets (the set of sets from A times the set of sets from B) gave the same, correct, set of eigenvalues.

This development leads us to conclude that once a correct set of signs is obtained for the RME's of a set of equivalent spins, then this set of signs will be correct for application to any system in which that set of spins occurs and, if desired, all the remaining correct sets can be generated, at will, as outlined above.

[1]R. L. Flurry, Jr. and T. H. Siddall III, in *Recent Advances in Group Theory,* edited by J. C. Donini (Plenum, New York, 1979).

[2]T. H. Siddall III and R. L. Flurry, Jr., J. Magn. Reson. **39**, 487 (1980).

[3]T. H. Siddall III and R. L. Flurry, Jr., J. Magn. Reson. **43**, 357 (1981).

[4]T. H. Siddall III, J. Phys. Chem. **36**, 91 (1982).

[5]W. E. Hatfield, in *Theory and Applications of Molecular Paramagnetism,* edited by E. A. Boudreaux and L. N. Mulay (Wiley, New York, 1976).

[6]J. S. Griffith, Struct. Bonding (Berlin) **10**, 87 (1972).

[7]B. G. Wybourne, *Symmetry Principles and Atomic Spectroscopy* (Wiley, New York, 1970).

[8]B. G. Wybourne, *Classical Groups for Physicists* (Wiley, New York, 1974).

[9]M. Hamermesh, *Group Theory and its Application to Physical Problems* (Addison-Wesley, Reading, Mass., 1962).

[10]B. L. Silver, *Irreducible Tensor Methods: An Introduction for Chemists* (Academic, New York, 1976).

[11]G. Racah, Phys. Rev. **62**, 438 (1942); **63**, 367 (1945); **73**, 1352 (1949).

[12]R. D. Kent, M. Schlesinger, and G. W. F. Drake, J. Comput. Phys. **40**, 430 (1981); R. D. Kent and M. Schlesinger, Phys. Rev. B **27**, 46 (1983); Pardu S. Ponnapalli, M. Schlesinger, and R. D. Kent, *ibid.* **31**, 1258 (1985); R. D. Kent, M. Schlesinger, and Pardu S. Ponnapalli, *ibid.* **31**, 1264 (1985).

[13]A de-Shalit and I. Talmi, *Nuclear Shell Theory* (Academic, New York, 1963).