

# Multilinear Interactions in High-Resolution Spectra

P. L. Corio

*Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055*

Received September 4, 1997; revised April 16, 1998

**The most general interaction of a collection of nuclear magnetic moments, invariant under the operations of the pure rotation group in three dimensions, is shown to be a linear combination of basic invariants that are multilinear in the components of the nuclear spin vectors. For an even number of spins each basic invariant is proportional to a product of scalar products, whereas for an odd number of spins each basic invariant is proportional to a scalar triple product multiplied by a product of scalar products. Representation theory for the group of proper rotations is used to determine the exact number of independent basic invariants for a given number of spins. The implications of time-reversal invariance and the consequences of including multilinear interactions in the Hamiltonian are investigated. In particular, the high-resolution spectrum of the AA'XX' system when quadrilinear interactions are included is examined.** © 1998 Academic Press

## INTRODUCTION

The fine structure observed in high-resolution spectra has been traditionally interpreted in terms of transitions between the energy levels of the Hamiltonian (*I*–7)

$$\mathcal{H} = -\sum_j \omega_j I_{zj} - \sum_{j < k} J_{jk} \mathbf{I}_j \cdot \mathbf{I}_k, \quad [1]$$

in which  $\hbar$  has been taken as the unit of angular momentum, so that the eigenvalues of  $\mathcal{H}$ , the  $\omega_j$ , and the  $J_{jk}$  are in angular frequency units.

The bilinear interactions—the second term of  $\mathcal{H}$ —represent the simplest, nontrivial rotationally invariant interactions of the nuclear moments (8, 9). There are, however, rotationally invariant *multilinear* interactions, and the question arises as to the necessity of including them in the Hamiltonian. The magnitudes of coupling constants associated with multilinear interactions are undoubtedly smaller than those associated with bilinear interactions, but there are instances where the magnitudes of bilinear coupling constants are considerable, and in such cases multilinear coupling constants could be appreciable. Furthermore, no systematic investigation as to the consequences of including multilinear interactions in the Hamiltonian has been re-

ported. Indeed, many characteristics of high-resolution spectra are consequences of rotational invariance, independent of the specific form of the interaction; and some characteristics of particular spin systems persist even when multilinear interactions are included. For example, the ABC system has the property that the spectrum may be divided into three quartets whose spacings sum to the absolute value of the sum of the bilinear coupling constants, and this property still holds when a terlinear interaction is included, since the latter makes no contribution to the diagonal elements of  $\mathcal{H}$ . It should not be concluded, however, that multilinear interactions are generally higher than first-order, for, as will be seen subsequently, quadrilinear interactions, among others, contribute to the diagonal elements of the Hamiltonian matrix.

## ROTATIONALLY INVARIANT INTERACTIONS

Let  $-V$  denote the most general rotationally invariant interaction of the nuclear moments, and write, for brevity,

$$Z = \sum_j \omega_j I_{zj}. \quad [2]$$

In this notation, the Hamiltonian is

$$\mathcal{H} = -(Z + V). \quad [3]$$

The interaction of  $N$  nuclear magnetic moments can be expanded in terms of a complete set of orthonormal operators, with the expansion coefficients subject to the conditions that  $V$  be Hermitian and rotationally invariant. This is somewhat analogous to the introduction of higher-order correction terms to the energy in other branches of spectroscopy, but the expansion here is exact and terminates after a finite number of terms.

Any operator defined on the states of angular momentum of a single nucleus with spin  $I$  may be expressed as a linear combination of the operators (*10*)

$$U_{\pm r}^{(n)} = (\pm 1)^n T_{\pm n}^{(r)}(II \pm I_0), \quad [4]$$

where

$$I_{\pm} = I_x \pm iI_y, \quad I_0 = I_z, \quad [5]$$

satisfying

$$[I_0, I_{\pm}] = \pm I_{\pm}, \quad [I_+, I_-] = 2I_0, \quad [6]$$

$I$  is the  $(2I + 1)$ -dimensional identity operator, and the  $Z_n^{(r)}(II \pm I_0)$ ,  $n = 0, 1, 2, \dots, 2I - r$ ,  $r = 0, 1, 2, \dots, 2I$ , are polynomials of degree  $n$  in  $I_0$ , obtained from the following (scalar) polynomial by replacing  $x$  with  $II \pm I_0$ :

$$\begin{aligned} Z_n^{(r)}(x) &= \left[ \binom{2n+2r}{n} \binom{2I+n+r+1}{2n+2r+1} \right]^{-1/2} \\ &\times \sum_{\nu=0}^n \frac{(-1)^{n+\nu} (n+r)!}{(n+2r)!} \binom{2I-r-\nu}{n-\nu} \\ &\times \binom{n+2r+\nu}{n+r} \binom{x}{\nu}. \end{aligned} \quad [7]$$

These polynomials satisfy the symmetry relation

$$Z_n^{(r)}(2I - r - x) = (-1)^n Z_n^{(r)}(x), \quad [8]$$

so that, when  $r = 0$ , the operators in Eq. [4] with the  $+$  sign are related to those with the  $-$  sign, and in this case only the  $2I + 1$  operators with the  $+$  (or  $-$ ) sign are to be taken. With this restriction, Eq. [4] generates a complete, orthonormal basis ( $I_0$ ) of  $(2I + 1)^2$  polynomial operators, whose overall degrees in  $I_0, I_+, I_-$  are given by the values of  $n + r$ . In particular, the (normalized) identity operator ( $n = r = 0$ ) is of degree zero. When  $r = 0$ , but  $n \neq 0$ , the operators are polynomials in  $I_0$ .

The  $U_{\pm r}^{(n)}$  satisfy the following relations:

$$U_{\pm r}^{(n)\dagger} = U_{\mp r}^{(n)}, \quad [9]$$

$$[I_0, U_{\pm r}^{(n)}] = \pm r U_{\pm r}^{(n)}, \quad [10]$$

$$[U_{\pm r}^{(n)}, I_{\pm}] = \pm [n(n+2r+1)]^{1/2} U_{\pm(r\pm 1)}^{(n-1)}, \quad [11]$$

$$[U_{\pm r}^{(n)}, I_{\mp}] = \pm [(n+1)(n+2r)]^{1/2} U_{\pm(r-1)}^{(n+1)}. \quad [12]$$

Equations [10]–[12] show that the  $U_{\pm r}^{(n)}$  are explicit realizations of the irreducible tensor operators,  $T_q^{(k)}$ , for the  $(2I + 1)$ -dimensional representation of the 3-dimensional rotation group, with  $n + r = k$ ,  $r = |q|$ .

In subscripts  $r$  is *always* a nonnegative integer, so that  $\pm r$  does not mean  $+r$  or  $-r$ , but merely distinguishes between the pair of operators with the  $+$  and  $-$  signs, both operators having the same value of  $r \geq 0$ ; in other instances, Eq. [10], for instance, the signs prefixed to the factor of  $r$  in the right member are algebraic. To distinguish the operators with the  $+$

and  $-$  signs, it will be convenient to use the symbol  $\epsilon$ , which may be  $+$  or  $-$ .

In the case of a composite system of  $N$  nuclei with spins  $I_1, I_2, \dots, I_N$ , Eqs. [6] hold for the corresponding operators of each spin vector  $\mathbf{I}_j = (I_{xj}, I_{yj}, I_{zj})$ , and also for those of the total spin vector

$$\mathbf{I} = \sum_{j=1}^N \mathbf{I}_j, \quad [13]$$

since operators for distinct nuclei commute. Henceforth,  $I_x, I_y, I_z = I_0, I_+, I_-$  refer to operators associated with the total spin vector  $\mathbf{I}$ ; the corresponding operators for the  $j$ th spin will be denoted  $I_{xj}, I_{yj}, I_{zj} = I_j^0, I_j^+, I_j^-$ .

An operator basis for the composite system is obtained by forming the  $\Pi_j(2I_j + 1)^2$  Kronecker products:

$$\prod_{j=1}^N U_{\epsilon_j r_j}^{(n_j)}, \quad [14]$$

where  $\epsilon_j = +$  or  $-$ , and the Kronecker products are serially ordered. The degree of a product operator is

$$d = \sum_{j=1}^N (n_j + r_j). \quad [15]$$

An arbitrary operator defined on the states of the composite spin system may be expressed as a linear combination of all possible products of the form [14]. The interaction operator  $V$  must be Hermitian and rotationally invariant, so that

$$V^\dagger = V, \quad [16]$$

$$\exp[-i\phi \mathbf{n} \cdot \mathbf{I}] V \exp[i\phi \mathbf{n} \cdot \mathbf{I}] = V, \quad [17]$$

where  $\mathbf{n}$  is an arbitrary unit vector along the axis of rotation, and  $\phi$  is the angle of rotation. Writing  $R$  for the rotation operator,  $\exp[-i\phi \mathbf{n} \cdot \mathbf{I}]$ , and  $R_j$  for the rotation  $\exp[-i\phi \mathbf{n} \cdot \mathbf{I}_j]$  on the subspace of spin  $j$ , a similarity transformation with  $R$  applied to a typical operator of the product basis yields

$$R \left( \prod_{j=1}^N U_{\epsilon_j r_j}^{(n_j)} \right) R^{-1} = \prod_{j=1}^N R_j U_{\epsilon_j r_j}^{(n_j)} R_j^{-1}. \quad [18]$$

The transformation of  $A^\alpha B^\beta$ , where  $A$  and  $B$  refer to spin  $j$ , may be carried out by means of the following rule:  $R_j A^\alpha B^\beta R_j^{-1} =$

$(R_j A R_j^{-1})^\alpha (R_j B R_j^{-1})^\beta$ . Now the operators for the individual spins are transformed into linear, homogeneous combinations of themselves under rotations. For example, under a rotation about the  $z$ -axis ( $I$ ),

$$\begin{aligned} \exp[-i\phi I_z] I_{\epsilon_j}^r \exp[i\phi I_z] &= (\exp[-i\phi I_{zj}] I_{\epsilon_j} \exp[i\phi I_{zj}])^{r_j} \\ &= \exp[-\epsilon_j r_j \phi] I_{\epsilon_j}^{r_j}. \end{aligned} \quad [19]$$

Thus, any operator of the product basis of given degree is transformed into a linear combination of products of the same degree, so that we may consider separately the rotational invariance of products having the same degree. The (normalized) identity operators,  $(2I_j + 1)^{-1/2} I_j$ , on the subspaces of the individual spins do not contribute to the overall degree of an operator product for the composite system.

The identity operator for the composite system is rotationally invariant and of degree zero, but as it would only add a constant to each eigenvalue of the Hamiltonian, it will be omitted. Operators of degree 1 are not rotationally invariant and, moreover, do not represent interactions. Interactions of degree 2, as we shall see subsequently, correspond to bilinear interactions, but for the construction of these and higher-order interactions, considerations of a general nature are necessary. Specifically, we examine the rotational invariance of  $V$  under infinitesimal rotations about the coordinate axes.

For an infinitesimal rotation  $\delta\phi$ , with  $\mathbf{n}$  taken successively as  $\mathbf{i}$ ,  $\mathbf{j}$ ,  $\mathbf{k}$ , Eq. [17] requires that

$$[V, I_x] = [V, I_y] = [V, I_z] = 0. \quad [20]$$

Conversely, if  $V$  commutes with each component of the total spin vector, it commutes with their positive integral powers and, therefore, with the rotation operator  $R$ . Now, it is easily shown that, if  $V$  commutes with  $A$  and  $B$ , it also commutes with  $[A, B]$ , so that if  $V$  commutes with any two of  $I_x, I_y, I_z$ , it will also commute with the third. We shall first determine those linear combinations of Kronecker products of a given degree that are invariant under rotations about the  $z$ -axis and are also Hermitian. The further requirement that they commute with  $I_+$  ensures their rotational invariance, for if these linear combinations commute with  $I_+$ , then, being Hermitian, they necessarily commute with  $I_-$  and, therefore, with  $I_x$  and  $I_y$ .

Consider then a linear combination of all product operators of a given degree  $d$ . Under a rotation about the  $z$ -axis, this combination will be subjected to a similarity transformation with  $\exp[-i\phi I_z]$ , and any product operator with all  $r_j = 0$  will be transformed into itself, as shown by Eq. [19]. On the other hand, any product operators for which not all  $r_j = 0$  will have

their  $+$  and  $-$  components subjected to transformation [19], and all such products will be transformed into themselves, provided that

$$\sum_{j=1}^N \epsilon_j r_j = 0. \quad [21]$$

Thus, in any product operator, the sum of the exponents of the  $I^+$  operators must equal the sum of the exponents of the  $I^-$  operators. It follows that

$$\sum_{j=1}^N r_j = 2\mu, \quad [22]$$

where  $\mu$  is a nonnegative integer. From Eqs. [15] and [22], we have

$$\sum_{j=1}^N n_j = d - 2\mu, \quad [23]$$

so that the parity of the sum of the  $n_j$  is odd or even with  $d$ .

Now consider a product operator of degree  $d$  for which not all  $r_j$  are zero, and let its coefficient be  $c$ . There is always another operator of the same degree in which the  $I^+$  and  $I^-$  operators are interchanged; let the coefficient of this operator be  $c'$ . Invariance under a rotation of  $180^\circ$  about the  $x$ -axis requires that

$$I_j^+ \rightarrow I_j^-, \quad I_j^- \rightarrow I_j^+, \quad I_j^0 \rightarrow -I_j^0, \quad [24]$$

so that the first product operator is transformed into the second, and vice versa, with a change of sign or not, according, by virtue of Eqs. [4] and [23], as  $d$  is odd or even. The condition of rotational invariance requires that  $c = -c'$  when  $d$  is odd, but  $c = c'$ , when  $d$  is even. Furthermore, as the Hermitian conjugate of  $A \otimes B \otimes C \otimes \dots$  is  $A^\dagger \otimes B^\dagger \otimes C^\dagger \otimes \dots$ , Eq. [16] requires that when  $d$  is even, the product operators for which not all  $r_j$  are zero are grouped into sums of conjugate pairs, multiplied by a single, real coefficient, whereas when  $d$  is odd, such products are grouped into differences of conjugate pairs, multiplied by a single, pure imaginary coefficient. The same conclusions hold in the case of product operators for which all  $r_j$  are zero, but when, in this case,  $d$  is odd, the coefficient of a product consisting entirely of  $z$ -components must vanish, by virtue of invariance under transformation [24]. This discussion also shows that there is always an odd number of product operators of a given degree.

## MULTILINEARITY OF THE INTERACTIONS

In any product operator, all operators other than normalized identity operators are of the first degree in the angular momentum operators. For in any product, there will be  $N - d$  normalized identity operators, and for these operators  $n_j = r_j = 0$ , so that the summation in Eq. [15] actually extends only over the values of  $n_j$  and  $r_j$  of those  $d$  operators other than normalized identity operators. If we suppose the that latter are the first  $d$  operators in each product, it follows that

$$\sum_{j=1}^d (n_j + r_j) = d. \quad [25]$$

But for the operators under consideration,  $n_j + r_j \geq 1$ , so that Eq. [25] requires  $n_j + r_j = 1$ , for all  $j = 1, 2, \dots, d$ . Consequently, either  $n_j = 1$  and  $r_j = 0$ , or  $n_j = 0$  and  $r_j = 1$ . Thus, the only operators that appear as factors in a Kronecker product are, except for normalization factors, the operators  $I_j^0, I_j^+, I_j^-$ , and identity operators for the individual spins. Hence, the interactions are *multilinear* in the angular momentum components of the nuclei. The degree  $d$  gives the order of the interaction: bilinear ( $d = 2$ ), terlinear ( $d = 3$ ), quadrilinear ( $d = 4$ ), etc. For brevity, normalization factors will be omitted, since the product operators retain their linear independence and orthogonality irrespective of these factors. We shall also use an abbreviated notation for ordered product operators, writing 0, +, - for spin  $j$ , according as the operator in the  $j$ th place is  $I_j^0, I_j^+,$  or  $I_j^-$ , omitting all identity operators, and enclosing the product in parentheses. For example, when  $N = 3$ ,  $(+ - 0)$  denotes the Kronecker product  $I_1^+ \otimes I_2^- \otimes I_3^0$ . The number of product operators of given degree  $d$ , containing  $n_+$  factors  $I_+$ ,  $n_- = n_+$  factors  $I_-$ , and  $n_0 = d - 2n_+$  factors  $I_0$  is

$$\eta(N, d, n_+) = \frac{N!}{(d - 2n_+)!(N - d)!(n_+!)^2}, \quad [26]$$

where  $n_+ = 0, 1, 2, \dots, d/2$  or  $(d - 1)/2$ , according as  $d$  is even or odd. For  $N = d = 2, 3, 4, 5, 6$ , Eq. [26] yields 3, 7, 19, 51, 141, respectively.

The preceding discussion leads to the following conclusions: (1) The form of the  $V$  is independent of the spin quantum numbers  $I_j$ , as the relations among the coefficients in the expansion for  $V$  are determined by the commutation relations alone. (2) The procedure outlined determines all rotationally invariant interactions, not all rotational invariants, the former being a subset of the latter. For instance, the identity operator, and the Kronecker product  $\prod_j \mathbf{I}_j^2$ , which is not, in general, a multiple of the identity operator, are

rotationally invariant, but do not represent interactions. (3) It may happen in particular instances that the components of certain angular momenta are quenched, and would thus not appear as factors in product operators. Such cases can only be considered as they arise, as particular details cannot be anticipated in a general argument.

## BASIC INVARIANTS OF LOW DEGREE

We now work out the form of the interactions for several cases, supposing that  $N = d$ . When  $N = d = 2$ , say spins 1 and 2, the interaction has the form  $a_{12}[(+-) + (-+)] + b_{12}(00)$ , since the coefficients of the first two operators must be equal, by the symmetry property mentioned previously. Setting the commutator with  $I_+ = I_1^+ + I_2^+$  equal to zero, we find that  $a_{12} = b_{12} \equiv J_{12}$ , so that  $V$ , in this case, is the familiar bilinear interaction  $J_{12} \mathbf{I}_1 \cdot \mathbf{I}_2$ .

For  $N = d = 3$ , say spins 1, 2, and 3, the interaction must be of the form

$$a[(+ - 0) - (- + 0)] + b[(+ 0 -) - (- 0 +)] + c[(0 + -) - (0 - +)].$$

Setting the commutator with  $I_+$  equal to zero, we find that  $a = -b = c$ , so there is only one independent constant, which must be pure imaginary for the interaction to be Hermitian. It follows that

$$\begin{aligned} V &= \frac{1}{2} i J_{123} [(+ - 0) - (- + 0) + (- 0 +) \\ &\quad - (+ 0 -) + (0 + -) - (0 - +)] \\ &= J_{123} \mathbf{I}_1 \cdot \mathbf{I}_2 \times \mathbf{I}_3, \end{aligned} \quad [27]$$

where  $J_{123}$  is real. It will be observed that this interaction does not contribute to the diagonal elements of  $\mathcal{H}$ , confirming the remarks made in the introduction regarding the properties of the ABC system.

When  $N = d = 4$ , similar calculations show that there are three independent interactions:

$$\begin{aligned} &\frac{1}{2} J_{1234} \{ (+ - 00) + (00 + -) + (00 - +) + (- + 00) \\ &\quad + \frac{1}{2} [(+ - + -) + (- + + -) + (- + - +) \\ &\quad + (+ - - +) + 4(0000)] \} \\ &= J_{1234} (\mathbf{I}_1 \cdot \mathbf{I}_2)(\mathbf{I}_3 \cdot \mathbf{I}_4), \end{aligned} \quad [28]$$

$$\begin{aligned}
 & \frac{1}{2}J_{1324}\{(+0-0) + (0+0-) + (0-0+) + (-0+0) \\
 & + \frac{1}{2}[(++--)+(-++-)+(--++) \\
 & + (+--+)+4(0000)]\} \\
 & = J_{1324}(\mathbf{I}_1 \cdot \mathbf{I}_3)(\mathbf{I}_2 \cdot \mathbf{I}_4), \tag{29}
 \end{aligned}$$

$$\begin{aligned}
 & \frac{1}{2}J_{1423}\{(+00-)+ (0+-0)+ (0-+0)+ (-00+) \\
 & + \frac{1}{2}[(++--)+(+--+)+(--++) \\
 & + (-+-+)+4(0000)]\} \\
 & = J_{1432}(\mathbf{I}_1 \cdot \mathbf{I}_4)(\mathbf{I}_2 \cdot \mathbf{I}_3), \tag{30}
 \end{aligned}$$

where the  $J$ 's are real constants. Other invariant interactions with four spins are expressible in terms of [28], [29], and [30]. For example,  $\mathbf{I}_1 \cdot [\mathbf{I}_2 \times (\mathbf{I}_3 \times \mathbf{I}_4)] = (\mathbf{I}_1 \cdot \mathbf{I}_3)(\mathbf{I}_2 \cdot \mathbf{I}_4) - (\mathbf{I}_1 \cdot \mathbf{I}_4)(\mathbf{I}_2 \cdot \mathbf{I}_3)$ . Quadrilinear interactions contribute to the diagonal elements of  $\mathcal{H}$  by virtue of the product operator (0000). For spin  $\frac{1}{2}$  nuclei, this product would multiply each coupling constant by a factor of  $\frac{1}{16}$ , which could lead to a considerable reduction in the contribution of a quadrilinear interaction to the energy.

### REDUCTION RELATIVE TO $O$ AND $O_3^+$

Although the preceding considerations, in principle, permit the determination of all rotationally invariant interactions, the algebra becomes increasingly arduous for larger values of  $N$ . The important conclusion that the interactions are multilinear in the angular momentum components may be combined with group theoretical considerations to provide further information regarding the formal aspects of the problem, and considerable simplification in the computations. In particular, we shall be able to determine the *exact* number of independent invariants for each  $N$ .

We begin by abandoning the expression of the invariants in terms of the  $+$ ,  $-$ ,  $0$  operators in favor of their expression in terms of the Cartesian components of the angular momenta. It is also convenient to adopt a concise notation for the products of angular momenta, writing, for example, when  $N = d = 5$ ,  $(xxyzx)$  for the Kronecker product  $I_{x1}I_{x2}I_{y3}I_{z4}I_{x5}$ . In general, there are  $3^N$  such products, all of which are Hermitian. We shall first adapt these products to the symmetries of the proper rotations of the octahedral group  $O$ , supposing the origin at the center of a cube, with the coordinate axes parallel its sides. Under any rotation, the components of angular momenta transform like vectors, and under the particular rotations of  $120^\circ$  and  $240^\circ$  about the cube diagonal extending from the origin to the vertex in the positive octant, the  $x$ ,  $y$ , and  $z$ -components of the angular momenta undergo cyclical permutations, so that, for any  $N$ , the invariants also have this property, and must

therefore belong to the totally symmetric representation  $A_1$  of the octahedral group, that is, each invariant spans a one-dimensional subspace.

The 24 proper rotations of the octahedral group belong to five classes:  $E$ ,  $8C_3$ ,  $3C_2$ ,  $6C_4$ ,  $6C_2'$ . The character table for the group is not required, as the characters for the  $A_1$  representation are all  $+1$ . The characters of the representation generated by the  $3^N$  product operators are  $\chi(E) = 3^N$ ,  $\chi(C_3) = 0$ ,  $\chi(C_4) = 1$ , for all  $N$ ,  $\chi(C_2) = \chi(C_2') = 1$ , for  $N$  even,  $-1$ , for  $N$  odd. With these results, a straightforward calculation shows that the number of linear combinations of products transforming according to the representation  $A_1$  of the octahedral group for several values of  $N$  is given in the following tabulation:

$N$	$3^N$	$O$	$O_3^+$
2	9	1	1
3	27	1	1
4	81	4	3
5	243	10	6
6	729	31	15
7	2187	91	36
8	6561	274	91
9	19,683	820	232
10	59,049	2,461	603

We can also reduce the product representation relative to the three-dimensional pure rotation group,  $O_3^+$ , whose irreducible representations are  $D_j$ , with  $j = 0, 1, 2, \dots$ , each of dimension  $2j + 1$ . Since the components of angular momenta transform like vectors, the products under consideration form a basis for  $D_1 \otimes D_1 \otimes D_1 \otimes \dots$  to  $N$  factors. Reducing this product into its irreducible components, using the Clebsch–Gordan series, we determine the number of times the one-dimensional representation  $D_0$  is contained in the product for each  $N$ . These numbers are given in the last column of the preceding tabulation.

To illustrate the calculation, consider the case  $N = d = 4$ . On applying the projection operator for the  $A_1$  representation of  $O$  to the 81 product operators, the following linear combinations of products transforming according to the  $A_1$  representation are obtained:

$$(xxxx) + (yyyy) + (zzzz), \tag{31}$$

$$(xxyy) + (yyzz) + (zzxx) + (xxzz) + (zzyy) + (yyzz), \tag{32}$$

$$(xyxy) + (yzzy) + (zxzx) + (xzxz) + (yxxy) + (zyzy), \tag{33}$$

$$(xyyx) + (yzzy) + (zxzx) + (xzxz) + (yxxy) + (zyzy). \tag{34}$$

Under reduction with respect to  $O_3^+$ , however, there are only three invariants. The reason is that reduction relative to  $O$  does not take into account *all* proper rotations. This means that after expressing  $V$  as a linear combination of the preceding four operators, we must evaluate additional commutators with, at most, two of  $I_x, I_y, I_z$ . It turns out that only the commutator with

$I_x$  is required, and on setting the result equal to zero, it is found the coefficient of [31] is equal to the sum of the coefficients of [32]–[34], leading to the three scalar products given in Eqs. [28]–[30]. It might be possible to avoid the evaluation of additional commutators by reducing the products relative to the proper rotations of the icosahedral group, but rotations about fivefold axes, which mix the components of angular momenta, would complicate the calculations.

When  $N = d = 5$ , the reduction with respect to  $O_3^+$  gives six as the number of independent invariants, and an explicit calculation discloses  $V$  as a linear combination of the following independent invariants:  $(\mathbf{I}_1 \cdot \mathbf{I}_2)(\mathbf{I}_3 \cdot \mathbf{I}_4 \times \mathbf{I}_5)$ ,  $(\mathbf{I}_1 \cdot \mathbf{I}_3)(\mathbf{I}_2 \cdot \mathbf{I}_4 \times \mathbf{I}_5)$ ,  $(\mathbf{I}_1 \cdot \mathbf{I}_4)(\mathbf{I}_2 \cdot \mathbf{I}_3 \times \mathbf{I}_5)$ ,  $(\mathbf{I}_1 \cdot \mathbf{I}_5)(\mathbf{I}_2 \cdot \mathbf{I}_3 \times \mathbf{I}_4)$ ,  $(\mathbf{I}_2 \cdot \mathbf{I}_3)(\mathbf{I}_1 \cdot \mathbf{I}_4 \times \mathbf{I}_5)$ ,  $(\mathbf{I}_2 \cdot \mathbf{I}_4)(\mathbf{I}_1 \cdot \mathbf{I}_3 \times \mathbf{I}_5)$ .

For  $N = d = 6$ , similar calculations lead to 15 independent invariants, as required under reduction relative to the pure rotation group; all of these invariants can be expressed as products of scalar products, such as  $(\mathbf{I}_1 \cdot \mathbf{I}_2)(\mathbf{I}_3 \cdot \mathbf{I}_4)(\mathbf{I}_5 \cdot \mathbf{I}_6)$ .

The preceding results parallel the theory of invariants under the  $n$ -dimensional orthogonal group: every invariant of even degree is expressible as a product of scalar products; every invariant of odd degree is expressible as a scalar triple product multiplied by scalar products (12).

### TIME-REVERSAL INVARIANCE

Invariance with respect to time reversal leads to a reduction in the number of coupling constants required in the high-resolution Hamiltonian for a multispin system. For under time reversal (13, 14), the components of angular momentum change sign, and the constant external magnetic field has its direction reversed. Assuming the Hamiltonian [3] is invariant under time reversal, the invariants of odd degree must be omitted from the Hamiltonian—

**TABLE 1**  
**Resonance Frequencies and Relative Intensities**  
**for the AA'XX' System:  $\mathcal{A}$  Transitions**

Frequency	Intensity
1. $\omega_A + \frac{1}{2}L_+ + \frac{1}{8}(J_{AXA'X'} + J_{AX'A'X})$	2
2. $\omega_A + \frac{1}{2}L_+ - \frac{1}{8}(J_{AXA'X'} + J_{AX'A'X})$	2
3. $\omega_A - \frac{1}{2}L_+ - \frac{1}{8}(J_{AXA'X'} + J_{AX'A'X})$	2
4. $\omega_A - \frac{1}{2}L_+ + \frac{1}{8}(J_{AXA'X'} + J_{AX'A'X})$	2
5. $\omega_A - \frac{1}{2}K_+ + \frac{1}{8}(2J_{AA'XX'} + J_{AXA'X'} + J_{AX'A'X}) + \frac{1}{2}R$	$\frac{2}{1+Q^2}$
6. $\omega_A - \frac{1}{2}K_+ + \frac{1}{8}(2J_{AA'XX'} + J_{AXA'X'} + J_{AX'A'X}) - \frac{1}{2}R$	$\frac{2Q^2}{1+Q^2}$
7. $\omega_A + \frac{1}{2}K_+ - \frac{1}{8}(2J_{AA'XX'} + J_{AXA'X'} + J_{AX'A'X}) + \frac{1}{2}R$	$\frac{2Q^2}{1+Q^2}$
8. $\omega_A + \frac{1}{2}K_+ - \frac{1}{8}(2J_{AA'XX'} + J_{AXA'X'} + J_{AX'A'X}) - \frac{1}{2}R$	$\frac{2}{1+Q^2}$

**TABLE 2**  
**Resonance Frequencies and Relative Intensities**  
**for the AA'XX' System:  $\mathcal{B}$  Transitions**

Frequency	Intensity
1. $\omega_A + \frac{1}{2}K_- - \frac{1}{8}(J_{AXA'X'} + J_{AX'A'X}) - \frac{1}{2}R'$	$\frac{2}{1+Q'^2}$
2. $\omega_A + \frac{1}{2}K_- - \frac{1}{8}(J_{AXA'X'} + J_{AX'A'X}) + \frac{1}{2}R'$	$\frac{2Q'^2}{1+Q'^2}$
3. $\omega_A - \frac{1}{2}K_- + \frac{1}{8}(J_{AXA'X'} + J_{AX'A'X}) - \frac{1}{2}R'$	$\frac{2Q'^2}{1+Q'^2}$
4. $\omega_A - \frac{1}{2}K_- + \frac{1}{8}(J_{AXA'X'} + J_{AX'A'X}) + \frac{1}{2}R'$	$\frac{2}{1+Q'^2}$

provided the coupling constants associated with these invariants are true scalars. Experimental evidence indicates that it is not necessary to include terlinear interactions in systems containing three or more spins, so that experimental investigations of multilinear interactions should begin with four-spin systems, and among these, the simplest would be the AA'BB' system, especially the limiting AA'XX' system, as the frequency separations of the resonances in the AA' and XX' regions are determined entirely by the coupling constants.

### THE AA'XX' SYSTEM

The spectrum of the AA' region of the AA'XX' system ( $C_2$  symmetry) when quadrilinear interactions are included is given in Tables 1 and 2, where

$$K_{\pm} = J_{AA'} \pm J_{XX'}, \quad L_{\pm} = J_{AX} \pm J_{AX'}$$

$$R = [(K_+ - \frac{1}{2}J_{AA'XX'} + L_-^2)^2]^{1/2}, \quad R' = [K_-^2 + L_-^2]^{1/2},$$

$$Q = -\frac{L_-}{K_+ - \frac{1}{2}J_{AA'XX'} + R}$$

$$Q' = -\frac{L_-}{K_- + R'}$$

The spectrum reduces to the conventional AA'XX' system (3, 6, 15) when all quadrilinear coupling constants vanish. In particular, the first and second  $\mathcal{A}$  transitions coalesce, as do the third and fourth  $\mathcal{A}$  transitions. As the predicted splitting of these lines has not been reported, it may be concluded that for known AA'XX' spectra either  $(J_{AXA'X'} + J_{AX'A'X})/4$  is negligibly small, or that  $J_{AXA'X'}$  and  $J_{AX'A'X}$  are comparable in magnitude but of opposite sign. If we set  $J_{AXA'X'} + J_{AX'A'X}$  equal to zero in Tables 1 and 2, we see that the spectrum is formally the same as the conventional AA'XX' system, except that  $K_+$  is replaced with  $K_+ - \frac{1}{2}J_{AA'XX'}$ . From this point of view, the customary interpretations of AA'XX' systems have

tacely assumed that  $J_{AA'XX'}$  is zero. For example, Smith and Ihrig (16) have studied 1,1-difluoroethylene in dimethyl sulfoxide, and from their data (17),

$$|J_{HH'} + J_{FF'} - \frac{1}{2}J_{HH'FF'}| = 30.45 \text{ Hz},$$

$$|J_{HH'} - J_{FF'}| = 41.20 \text{ Hz}.$$

Removing the signs of absolute value, we find the following values (in hertz):

$$J_{HH'} = -5.37 + \frac{1}{4}J_{HH'FF'},$$

$$J_{FF'} = 35.82 + \frac{1}{4}J_{HH'FF'},$$

which reduce to the values of Smith and Ihrig for  $J_{HH'}$  and  $J_{FF'}$  when  $J_{HH'FF'} = 0$ . The analysis of Smith and Ihrig is in excellent agreement with the experimental data, but the fit would be unaltered by assigning *any* value, positive or negative, to  $J_{HH'FF'}$ , as the values of  $|K_+|$  and  $|K_-|$  would also be unaltered.

It would appear that the question of multilinear interactions could be settled by theoretical calculations of multilinear coupling constants, by the examination of AA'XX' spectra in cases where the bilinear couplings constants are large, looking in particular for a splitting or unusual broadening of the normally coalesced  $\mathcal{A}$  transitions, or by experimental methods designed to detect small coupling constants.

## REFERENCES

1. E. L. Hahn and D. E. Maxwell, *Phys. Rev.* **84**, 1246 (1951).
2. H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.* **21**, 279 (1953).
3. H. M. McConnell, A. D. McClean, and C. A. Reilly, *J. Chem. Phys.* **23**, 68 (1955).
4. W. A. Anderson, *Phys. Rev.* **102**, 151 (1956).
5. J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," Chapter 6, McGraw-Hill, New York (1959).
6. P. L. Corio, *Chem. Rev.* **60**, 363 (1960).
7. P. L. Corio, "Structure of High-Resolution NMR Spectra," Academic Press, New York (1966).
8. E. L. Hahn, *Phys. Rev.* **80**, 580 (1950).
9. H. S. Gutowsky and D. W. McCall, *Phys. Rev.* **82**, 748 (1951).
10. P. L. Corio, *J. Math. Phys.* **9**, 1067 (1968).
11. Reference 7, p. 66.
12. H. Weyl, "The Classical Groups, Their Invariants and Representations," Chapter II, Theorem (2.9.A). Princeton (1946).
13. E. P. Wigner, "Group Theory," Chapter 26, Academic Press, New York (1959).
14. R. G. Sachs, "The Physics of Time Reversal," Chapter 3, Chicago (1987).
15. Reference 7, p. 384.
16. S. L. Smith and A. M. Ihrig, *J. Chem. Phys.* **46**, 1181 (1967).
17. A. M. Ihrig, Thesis, p. 206, University of Kentucky (1966).