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## Reduction tables for tensorial products of irreducible tensor operators $O^{(k)}(J)$ used in spectroscopy

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**Abstract.** Double and multiple irreducible products of irreducible tensor operators  $O^{(k)}(J)$  obeying special commutation relations arising from the properties of angular momentum operators are considered. It is shown that the double product can be expressed in terms of another set  $O^{(k)}$  associated with a coupling coefficient  $\varepsilon_k^{(k_1, k_2)}$  defined by  $[O^{(k_1)} \times O^{(k_2)}]^{(k)} = \varepsilon_k^{(k_1, k_2)} O^{(k)}$ . An analytical expression has been derived for the coupling coefficient  $\varepsilon_k^{(k_1, k_2)}$  and its values are tabulated for  $k_1$  and  $k_2$  up to 3. It is proved that  $[O^{(k_1)} \times O^{(k_2)}]^{(k)} = [O^{(k_2)} \times O^{(k_1)}]^{(k)}$ . Multiple irreducible products are also discussed. The coupling coefficients for triple products are tabulated for  $\Sigma_i k_i$  up to 6. Some important special cases of quadruple products are dealt with explicitly. Applications of the present results to high-order effects in spectroscopy are investigated.

### 1. Introduction

The theory of irreducible tensorial sets originated by Racah (see, e.g., [1]) is very useful in nuclear, atomic, molecular and solid state spectroscopies and has been greatly developed during the last decades (see, e.g., [2–4] and references therein). In particular, the operator equivalents [5–7] have proved to be extremely fruitful for the understanding of the magnetic and optical properties of  $d^N$  and  $f^N$  open-shell ions in crystalline materials [8–10].

There are some problems which require taking into account higher-order effects associated with a given interaction. One example is the higher-order exchange interaction in the theory of high-temperature susceptibility of Heisenberg ferromagnets, which is not negligible for many substances [11, 12]. In the microscopic spin-Hamiltonian theory used in EPR spectroscopy [9] as well as in NMR spectroscopy [13] and in the study of optical transitions [14–16], one needs to consider perturbations of second and higher orders, which give rise to the products of irreducible tensor operators.

The present paper deals with irreducible products of irreducible tensor operators  $O^{(k)}(J)$  obeying special commutation relations arising from the properties of angular momentum operators and which are extensively used in the crystal field analysis and the spin-Hamiltonian formalism. After presenting basic definitions in section 2 we calculate the coupling coefficients and discuss their symmetry properties in sections 3 and 4 for

two and three (or more) irreducible tensorial sets, respectively. Section 5 deals with applications of the present results.

## 2. Basic definitions

A set of irreducible tensor operators  $T_q^{(k)}$ ,  $q = k, k-1, \dots, -k$ , is defined by the commutation relations [1]

$$[J_{\pm}, T_q^{(k)}] = [k(k+1) - q(q \pm 1)]^{1/2} T_{q \pm 1}^{(k)} \quad (1)$$

$$[J_z, T_q^{(k)}] = q T_q^{(k)} \quad (2)$$

where  $J_z$  and  $J_{\pm} \equiv J_x \pm iJ_y$  are the angular momentum operators.

Buckmaster [7], and later independently Smith and Thornley [6], defined the irreducible tensor operators  $O_q^{(k)}(J)$  in such a way that for  $q = k$  the following relation holds [17]

$$O_k^{(k)} = [(-1)^k / 2^k k!] [(2k)!]^{1/2} J_+^k. \quad (3)$$

The operators  $O_q^{(k)}$  defined by (3) have been tabulated for all values of  $k$  up to  $k = 6$  [7] and  $k = 8$  [17, 18]. A comprehensive discussion of Buckmaster and Smith-Thornley (BST) operators and other operators used in the crystal-field and EPR areas as well as their properties can be found in the review in [19]. It should be mentioned that the operators most widely used in these areas, namely the extended Stevens (ES) operators [20, 21] are not of spherical but of tesseral type. Transformation relations between various tensor operators can be found in [19].

The matrix elements of  $O^{(k)}$  in (3) are given by [22]

$$\langle JM | O_q^{(k)} | J' M' \rangle = (-1)^{J-M} \begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \langle J || O^{(k)} || J \rangle \delta_{JJ'} \quad (4)$$

where the reduced matrix element is defined as

$$\langle J || O^{(k)} || J \rangle = (1/2^k) [(2J+k+1)/(2J-k)!]^{1/2}. \quad (5)$$

The irreducible product of two tensorial sets  $A_{q_1}^{(k_1)}$  and  $B_{q_2}^{(k_2)}$  is defined, using the 3j-symbols, as follows [1]:

$$[A^{(k_1)} \times B^{(k_2)}]_q^{(k)} = \sum_{q_1 q_2} (-1)^{k_1 - k_2 + q} (2k+1)^{1/2} \begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & -q \end{pmatrix} A_{q_1}^{(k_1)} B_{q_2}^{(k_2)}. \quad (6)$$

When the two sets  $A^{(k_1)}$  and  $B^{(k_2)}$  commute with each other,  $[B^{(k_2)} \times A^{(k_1)}]_q^{(k)}$  differs from  $[A^{(k_1)} \times B^{(k_2)}]_q^{(k)}$  by a factor  $(-1)^{k_1 + k_2 - k}$ , as follows from the properties of the 3j symbols.

In the case when  $A^{(k_1)} \equiv O^{(k_1)}$  and  $B^{(k_2)} \equiv O^{(k_2)}$ , the coupling shows more interesting features owing to the non-commutation of the operator sets. First of all, the irreducible product can be expressed in terms of  $O_q^{(k)}$  as follows:

$$[O^{(k_1)} \times O^{(k_2)}]_q^{(k)} = \varepsilon_k^{(k_1, k_2)} O_q^{(k)} \quad (7)$$

where  $|k_1 - k_2| \leq k \leq k_1 + k_2$ . Since the coupling coefficient  $\varepsilon_k^{(k_1, k_2)}$  defined by (7) is independent of  $q$  (see section 3), we may rewrite equation (7) in the form

$$[O^{(k_1)} \times O^{(k_2)}]^{(k)} = \varepsilon_k^{(k_1, k_2)} O^{(k)}. \quad (8)$$

### 3. Coupling of two irreducible tensorial sets

It is useful for many purposes to know the numerical values of the coupling coefficient  $\varepsilon_k^{(k_1, k_2)}$  defined in (7). One way to calculate these values is to use the explicit form of  $O_q^{(k)}$ , to expand the left-hand side of (7) according to (6) and to apply repeatedly the commutation relations (1) and (2). This method has been used previously by one of us [23–25]. In fact, equations (1) and (2) have to be used to reduce the ranks of the operators when  $k < k_1 + k_2$ , and this reduction becomes possible when  $J \cdot J (=J_x^2 + J_y^2 + J_z^2)$  occurs. Thus, if the coupling coefficient  $\varepsilon_k^{(k_1, k_2)}$  depends on  $J$ , it must exhibit the  $J(J + 1)$ -dependence, where  $J(J + 1)$  is the eigenvalue of  $J \cdot J$ . Using this method, some coefficients for lower values of  $k_i$  ( $i = 1, 2$ ) have been calculated and applied to the spin-Hamiltonian theory of  $3d^4$  and  $3d^6$  ions [23–26].

In this paper, a more general approach for calculating the required coupling coefficients is presented. This method is based on the application of the Wigner theorem in equation (4) to both sides of equation (7). Using (5) and the expression for the reduced matrix element  $\langle J || O^{(k_1)} \times O^{(k_2)} || J \rangle$  (see, e.g., [22]), one obtains

$$\varepsilon_k^{(k_1, k_2)} = (-1)^{2J+k} (2k + 1)^{1/2} \begin{Bmatrix} k_1 & k_2 & k \\ J & J & J \end{Bmatrix} \times \left( \frac{(2J + k_1 + 1)!(2J + k_2 + 1)!(2J - k)!}{(2J - k_1)!(2J - k_2)!(2J + k + 1)!} \right)^{1/2} 2^{k-k_1-k_2} \tag{9}$$

where  $\{ \dots \}$  denotes the  $6j$ -symbols. Hence, it follows from (9) that  $\varepsilon_k^{(k_1, k_2)}$  is independent of  $q$ . However, it depends, in general, on the  $J$ -value, showing the  $J(J + 1)$ -dependence discussed above. The relation equivalent to (9) has been derived by Schwinger (see [2], p 267) and Judd (see [3], p 102), albeit in different operator notation.

An important property of  $\varepsilon_k^{(k_1, k_2)}$  follows from the symmetry properties of the  $6j$ -symbols [27]; we obtain

$$\varepsilon_k^{(k_1, k_2)} = \varepsilon_k^{(k_2, k_1)} \tag{10}$$

The symmetry property (10) implies that

$$[O^{(k_1)} \times O^{(k_2)}]^{(k)} = [O^{(k_2)} \times O^{(k_1)}]^{(k)} \tag{11}$$

This is to be compared with a similar expression for the irreducible tensorial sets  $A^{(k_1)}$  and  $B^{(k_2)}$  of commuting tensor operators [1]

$$[A^{(k_1)} \times B^{(k_2)}]^{(k)} = (-1)^{k_1+k_2-k} [B^{(k_2)} \times A^{(k_1)}]^{(k)} \tag{12}$$

and with the corresponding expressions for the eigenstates of the total angular momentum  $j = j_1 + j_2$  [1]

$$|j_1 j_2 jm\rangle = (-1)^{j_1+j_2-j} |j_2 j_1 jm\rangle \tag{13}$$

The difference between the coupling of sets of operators which commute with each other (12), discussed in detail in [1], and that of the irreducible operators  $O^{(k_1)}(J)$  operators (11) is very evident. The related symmetry property of  $\varepsilon_k^{(k_1, k_2)}$  in equation (10) is useful since it enables us to reduce considerably the tables of the coefficients  $\varepsilon_k^{(k_1, k_2)}$ . In table 1 we list values of  $\varepsilon_k^{(k_1, k_2)}$  for  $k_1$  and  $k_2 = 1, 2$  and 3. These values have been numerically checked by a FORTRAN program.

Another useful symmetry relationship can be obtained by interchanging  $k_2$  and  $k$  in (9):

$$\varepsilon_k^{(k_1, k_2)} = A(k_2, k) \varepsilon_{k_2}^{(k_1, k)} \quad (14)$$

where

$$A(k_2, k) = [A(k, k_2)]^{-1} = (-1)^{k-k_2} (2k+1)^{1/2} 4^k (2J+k_2+1)! (2J-k)! \\ \times [(2k_2+1)^{1/2} 4^{k_2} (2J+k+1)! (2J-k_2)!]^{-1}. \quad (15)$$

It is easy to show that, when  $k = k_1 + k_2$  and  $k = k_1 + k_2 - 1$ ,  $\varepsilon_k^{(k_1, k_2)}$  is independent of  $J$ . In fact, we have, from (9),

$$\varepsilon_{k_1+k_2}^{(k_1, k_2)} = [(k_1+k_2)!/k_1!k_2!] [(2k_1)!(2k_2)!/(2k_1+2k_2)!]^{1/2} \quad (16)$$

$$\varepsilon_{k_1+k_2-1}^{(k_1, k_2)} = -[(k_1+k_2)!/(k_1-1)!(k_2-1)!] \{[(2k_1-1)!(2k_2-1)!/(2k_1+2k_2)!] \\ \times (2k_1+2k_2-1)\}^{1/2} \quad (17)$$

$$\varepsilon_{k_1-k_2}^{(k_1, k_2)} = (-1)^{k_2} \{(2J-k_1+k_2)!(2J+k_1+1)!k_1! \\ \times [2^{2k_2}(2J+k_1-k_2+1)!(k_1-k_2)!k_2!(2J-k_1)!]^{-1}\} \\ \times [(2k_1-2k_2+1)!(2k_2)!/(2k_1+1)!]^{1/2} \quad (18)$$

$$\varepsilon_{k_1-k_2+1}^{(k_1, k_2)} = (-1)^{k_2} \{(2J+k_1+1)!(2J+k_2-k_1-1)!(k_1+1)! \\ \times [4^{k_2-1}(2J+k_1+2-k_2)!(2J-k_1)!(k_2-1)!(k_1-k_2)!]^{-1}\} \\ \times [(2k_2-1)!(2k_1-2k_2+1)!(2k_1-2k_2+3)/(2k_1+2)!]^{1/2} \quad (19)$$

$$\varepsilon_k^{(k_1, 0)} = \delta_{k_1 k}. \quad (20)$$

We have assumed that  $k_1 \geq k_2$  in the derivation of relations (18) and (19).

#### 4. Multiple products of irreducible tensorial sets

We have shown in the preceding section that  $[O^{(k_1)} \times O^{(k_2)}]^{(k)}$  can be expressed in terms of  $O^{(k)}$  and is actually equal to  $[O^{(k_2)} \times O^{(k_1)}]^{(k)}$  because of the symmetry property of the coupling coefficient  $\varepsilon_k^{(k_1, k_2)}$ . For three or more irreducible tensorial sets of degrees  $k_1, k_2, k_3, \dots, k_i$ , there exist more than one distinct coupling schemes. In a similar way to equation (8), we can express a multiple product of degree  $k$  in terms of  $O^{(k)}$  associated with a coupling coefficient, which depends, in general, on the coupling scheme. In other words, different coupling schemes produce, in general, different products.

Let us introduce the following short-hand notation:

$$\{O^{(k_a)} \times O^{(k_b)}\} \equiv \sum_n [O^{(k_a)} \times O^{(k_b)}]^{(n)} \quad (21)$$

where  $n$  takes values from  $|k_a - k_b|$  to  $k_a + k_b$ . There are three coupling schemes in the case of a triple product, namely  $\{[O^{(k_1)} \times O^{(k_2)}] \times O^{(k_3)}\}^{(k)}$ ,  $\{[O^{(k_2)} \times O^{(k_3)}] \times O^{(k_1)}\}^{(k)}$  and  $\{[O^{(k_1)} \times O^{(k_3)}] \times O^{(k_2)}\}^{(k)}$ . For each of three schemes we may apply (8) repeatedly to obtain the respective coupling coefficients, denoted as

$\varepsilon_k^{[(k_1 k_2) k_3]}$ ,  $\varepsilon_k^{[(k_2 k_3) k_1]}$  and  $\varepsilon_k^{[(k_1 k_3) k_2]}$ . For example, we have

$$[[O^{(k_1)} \times O^{(k_2)}] \times O^{(k_3)}]^{(k)} = \varepsilon_k^{[(k_1 k_2) k_3]} O^{(k)} \tag{22}$$

where

$$\varepsilon_k^{[(k_1 k_2) k_3]} = \sum_n \varepsilon_n^{(k_1, k_2)} \varepsilon_k^{(n, k_3)} \tag{23}$$

and  $n = |k_1 - k_2|, |k_1 - k_2| + 1, \dots, k_1 + k_2$ . There are more possible coupling schemes in the case of quadruple products. Similarly, in this case we have explicitly, for example,

$$\sum_{n_1 n_2} [[O^{(k_1)} \times O^{(k_2)}]^{(n_1)} \times [O^{(k_3)} \times O^{(k_4)}]^{(n_2)}]^{(k)} = \varepsilon_k^{[(k_1 k_2) (k_3 k_4)]} O^{(k)} \tag{24}$$

where

$$\varepsilon_k^{[(k_1 k_2) (k_3 k_4)]} = \sum_{n_1 n_2} \varepsilon_{n_1}^{(k_1, k_2)} \varepsilon_k^{(n_1, n_2)} \varepsilon_{n_2}^{(k_3, k_4)} \tag{25}$$

and the summation is over  $n_1 = |k_1 - k_2|$  to  $k_1 + k_2$  and  $n_2 = |k_3 - k_4|$  to  $k_3 + k_4$ .

It is seen from (23) and (24) that the coupling coefficients of three or more sets are determined by  $\varepsilon_k^{(k_1, k_2)}$ , i.e. the coupling coefficients for the double sets. Table 2 lists the values of  $\varepsilon_k^{[(k_1 k_2) k_3]}$  for  $\sum_i k_i$  up to 6. These values have been numerically checked by a FORTRAN program. For quadruple products, we calculate  $\varepsilon_k^{[(k_1 k_2) (k_3 k_4)]}$  only for the case  $k_1 = k_2 = k_3 = k_4 = 1$ , which is of direct importance for the microscopic spin-Hamiltonian theory [26]. We obtain

$$\begin{aligned} \varepsilon_0^{[(11)(11)]} &= \frac{1}{6}[7 + 2J^2(J + 1)^2] \\ \varepsilon_1^{[(11)(11)]} &= -1/2\sqrt{2} + (\sqrt{6}/3)J(J + 1) + [(6 + \sqrt{3})/6\sqrt{30}][4J(J + 1) - 3] \\ \varepsilon_2^{[(11)(11)]} &= \sqrt{2} + 1/\sqrt{6} - (2\sqrt{2}/3)J(J + 1) - (1/3\sqrt{14})[4J(J + 1) - 15] \\ \varepsilon_3^{[(11)(11)]} &= -(2/\sqrt{5})(1 + \sqrt{2}) \\ \varepsilon_4^{[(11)(11)]} &= 2\sqrt{70}/35. \end{aligned} \tag{26}$$

The results for  $\varepsilon_k^{[(11)(11)]}$ ,  $k = 2$  and 4, have been calculated independently by Rudowicz [23].

It is worthwhile mentioning that there exist special cases where different coupling schemes lead to the same irreducible product. Then, the coupling relation may be written as

$$[O^{(k_1)} \times O^{(k_2)} \times \dots \times O^{(k_n)}]^{(k)} = \varepsilon_k^{[k_1 k_2 \dots k_n]} O^{(k)}. \tag{27}$$

This applies to the following cases:

- (i)  $k = k_1 + k_2 + \dots + k_n$ ,
- (ii)  $k = 0$  and  $k_1 = k_2 = k_3$  for the triple products and
- (iii)  $k = 0$  and  $k_1 = k_2 = k_3 = k_4$  for the quadruple products.

Then, we obtain

$$\begin{aligned} \varepsilon_{k_1+k_2+\dots+k_n}^{[k_1 k_2 \dots k_n]} &= [(k_1 + k_2 + \dots + k_n)! / k_1! k_2! \dots k_n!] \\ &\times [(2k_1)!(2k_2)! \dots (2k_n)! / (2k_1 + 2k_2 + \dots + 2k_n)!]^{1/2} \end{aligned} \tag{28}$$

Table 1. Coupling coefficients  $\epsilon_k^{(k_1, k_2)}$ . The coefficients enclosed in boxes have been derived independently by Rudowicz [23] by repeated application of the commutation relations (1) and (2) without using the general relation (9).  $J^*$  denotes  $J(J+1)$ .

$k_1$	$k_2$	$k = 0$	$k = 1$	$k = 2$	$k = 3$	$k = 4$	$k = 5$	$k = 6$
1	1	$\frac{1}{\sqrt{3}} J^*$	$-\frac{1}{\sqrt{2}}$	$\frac{\sqrt{2}}{\sqrt{3}}$				
2	1	0	$-\frac{1}{2\sqrt{10}}(4J^*-3)$	$-\sqrt{2}$	$\frac{3}{\sqrt{5}}$			
2	2	$\frac{J^*}{4\sqrt{5}}(4J^*-3)$	$\frac{3}{4\sqrt{10}}(4J^*-3)$	$-\frac{1}{2\sqrt{14}}(4J^*-15)$	$-\frac{6}{\sqrt{10}}$	$\frac{2}{3\sqrt{35}}$		
3	1	0	0	$-\frac{3}{\sqrt{21}}(J^*-2)$	$-\sqrt{3}$	$\frac{2}{\sqrt{7}}$		
2	2	0	$\frac{3}{4\sqrt{35}}(J^*-2)(4J^*-3)$	$\frac{6}{\sqrt{14}}(J^*-2)$	$-\frac{1}{2\sqrt{15}}(4J^*-33)$	$-3\sqrt{\frac{5}{7}}$	$\frac{\sqrt{10}}{\sqrt{21}}$	
3	3	$-\frac{J^*}{4\sqrt{7}}(J^*-2)(4J^*-3)$	$-\frac{3}{4\sqrt{7}}(J^*-2)(4J^*-3)$	$\frac{1}{2\sqrt{21}}(J^*-2)(4J^*-33)$	$\frac{3}{\sqrt{6}}(2J^*-9)$	$-\frac{6}{\sqrt{154}}(J^*-17)$	$-\frac{15}{\sqrt{21}}$	$\frac{10}{\sqrt{731}}$

$$\varepsilon_0^{[k_1 k_2 k_3]} = \varepsilon_{k_3}^{(k_1, k_2)} A(k_3, 0) \tag{29}$$

$$\varepsilon_k^{[(k_1 k_1 k_1)]} = \sum_n \varepsilon_n^{(k_1, k_1)} \varepsilon_k^{(n, k_1)} \tag{30}$$

$$\varepsilon_0^{[k_1 k_1 k_1 k_1]} = \sum_n [\varepsilon_n^{(k_1, k_1)}]^2 A(n, 0). \tag{31}$$

### 5. Applications

Several interactions considered in nuclear, atomic, molecular and solid state spectroscopies can be expressed in terms of irreducible tensor operators. Higher-order effects due to these interactions often play an important role. A typical example is the zero-field splitting (ZFS) in EPR spectroscopy of  $d^N$  and  $f^N$  ions in crystals. For  $d^N$  ions, the ZFS arises from the second- and higher-order perturbation with respect to the spin-orbit interaction given within an  $LS$  term by

$$\mathcal{H}_{so} = \lambda L \cdot S = \lambda O^{(1)}(L) \cdot O^{(1)}(S) \tag{32}$$

as well as the electronic spin-spin coupling

$$\mathcal{H}_{ss} = -\rho[(L \cdot S)^2 + \frac{1}{2}L \cdot S - \frac{1}{3}L(L + 1)S(S + 1)] \tag{33}$$

(see, e.g., [26]). In NMR spectroscopy of crystals containing lanthanide ions, higher-order effects of the hyperfine interaction  $AJ \cdot I$  and the quadrupole coupling  $C[2(J \cdot I)^2 + J \cdot I - \frac{2}{3}J(J + 1)I(I + 1)]$  produce a splitting similar to that of the ZFS in EPR [13]. In the case of ferromagnetics, the higher-order exchange interaction  $A_n(S_i \cdot S_j)^n$  with  $n > 1$  is not negligible for the high-temperature susceptibility [11, 12]. In dealing with these problems we often need to consider multiple products of scalar products such as  $(A^{(k_1)} \cdot B^{(k_1)})(A^{(k_2)} \cdot B^{(k_2)})$ . A recoupling procedure for this type of product has been considered by Fano and Racah [1], who derived the following relation:

$$(A^{(k_1)} \cdot B^{(k_1)})(A^{(k_2)} \cdot B^{(k_2)}) = \sum_k (-1)^{k_1 + k_2 - k} [A^{(k_1)} \times A^{(k_2)}]^{(k)} \cdot [B^{(k_1)} \times B^{(k_2)}]^{(k)} \tag{34}$$

where  $A^{(k_i)}$  and  $B^{(k_i)}$ ,  $i = 1$  and  $2$ , are irreducible tensor operators defined with the Condon-Shortley [28] phase convention ( $A_0^{(1)} \sim z$ ), which has been adopted by Buckmaster [7], by Smith and Thornley [6] as well as in this work. When the Fano-Racah [1] phase convention ( $\tilde{A}_0^{(1)} \sim iz$ ) is adopted, the phase factor  $(-1)^{k_1 + k_2 - k}$  must be omitted in (34). A generalization of equation (34) to multiple products and its graphical representation has been provided by Rudowicz [25]. Using equation (34) and the values of  $\varepsilon_k^{(1,1)}$  ( $k = 0, 1, 2$ ) listed in table 1,  $\mathcal{H}_{ss}$  (33) can be rewritten [25] as

$$\mathcal{H}_{ss} = -\frac{2}{3}\rho O^{(2)}(L) \cdot O^{(2)}(S) = \frac{2}{3}\rho \sum_q (-1)^q O_q^{(2)}(L) O_{-q}^{(2)}(S). \tag{35}$$

A similar expression can be obtained for the hyperfine quadrupole interaction with  $C$  replacing  $-\rho$  in (35). The form (35) facilitates application of the Wigner theorem (4) to calculate the matrix element of  $\mathcal{H}_{ss}$  within the basis of the ‘uncoupled’ functions  $|LM_L SM_S\rangle \equiv |LM_L\rangle |SM_S\rangle$ .

Equation (35) facilitates also derivation by tensorial algebra of the spin-spin coupling and mixed spin-spin coupling and spin-orbit coupling contributions to the spin Hamiltonian considered first by Rudowicz [25] (cf also [26]). As an example, we consider here,



Table 2. Coupling coefficients  $\epsilon_k^{(k_1 k_2 k_3)}$ . Values in boxes have been calculated independently by Rudowicz [23].  $J^*$  denotes  $J(J+1)$ .

$k_1$	$k_2$	$k_3$	$k=0$	$k=1$	$k=2$
1	1	1	$\frac{J^*}{\sqrt{6}}$	$\frac{J^*}{\sqrt{3}} + \frac{4J^*-3}{2\sqrt{15}}$	$-\left(1 + \frac{1}{\sqrt{3}}\right)$
1	1	2	$\frac{J^*(4J^*-3)}{2\sqrt{30}}$	$\frac{1+\sqrt{3}}{4\sqrt{5}}(4J^*-3)$	$-\frac{J^*}{\sqrt{3}}\left(1 + \frac{2}{\sqrt{7}}\right) + \frac{\sqrt{3}}{2} + \frac{15}{2\sqrt{21}}$
1	2	1	$\frac{J^*(4J^*-3)}{2\sqrt{30}}$	$\frac{1+\sqrt{3}}{4\sqrt{5}}(4J^*-3)$	$-\frac{4J^*-3}{2\sqrt{15}} - \frac{3(J^*-2)}{\sqrt{35}} + 2$
1	2	2	$-\frac{\sqrt{3}J^*(4J^*-3)}{4\sqrt{30}}$	$(4J^*-3)\left[\frac{4J^*-3}{40} + \frac{9}{8\sqrt{15}} + \frac{9(J^*-2)}{20\sqrt{21}}\right]$	$\frac{3(4J^*-3)}{4\sqrt{15}} + \frac{3(4J^*-15)}{4\sqrt{21}} + \frac{18(J^*-2)}{\sqrt{210}}$
2	2	1	$-\frac{3J^*(4J^*-3)}{4\sqrt{30}}$	$\frac{4J^*-3}{8\sqrt{5}}\left[2J^*-3 + \frac{4J^*-15}{\sqrt{7}}\right]$	$\frac{3(4J^*-3)}{4\sqrt{15}} + \frac{3(4J^*-15)}{4\sqrt{21}} + \frac{18(J^*-2)}{\sqrt{210}}$
2	2	2	$-\frac{J^*(4J^*-15)(4J^*-3)}{8\sqrt{70}}$	$-(4J^*-3)\left[\frac{3(4J^*-3)}{80} + \frac{3(4J^*-15)}{16\sqrt{35}} + \frac{9(J^*-2)}{10\sqrt{14}}\right]$	$\frac{(4J^*-3)(2\sqrt{3}J^*-9)}{8\sqrt{15}} + \frac{3(J^*-2)}{14\sqrt{5}} + \frac{(4J^*-15)^2}{56}$

Table 2—continued.

$k_1$	$k_2$	$k_3$	$k = 3$	$k = 4$	$k = 5$	$k = 6$
1	1	1	$\frac{\sqrt{2}}{\sqrt{5}}$			
1	1	2	$-\frac{3}{\sqrt{30}}(1+2\sqrt{2})$	$\frac{6}{\sqrt{105}}$		
1	2	1	$-\frac{3}{\sqrt{10}}(1+\sqrt{2})$	$\frac{6}{\sqrt{105}}$		
1	2	2	$\frac{9}{\sqrt{15}} - \frac{3(4J^*-3)}{10\sqrt{6}} - \frac{1}{10}(4J^*-33)$	$-\frac{9(1+\sqrt{5})}{\sqrt{105}}$	$\sqrt{\frac{2}{7}}$	
2	2	1	$\frac{18}{\sqrt{30}} - \frac{4J^*-15}{2\sqrt{70}}(\sqrt{3}+2)$	$-\frac{6(2+\sqrt{5})}{\sqrt{70}}$	$\sqrt{\frac{2}{7}}$	
2	2	2	$\frac{9(4J^*-3)}{20\sqrt{6}} + \frac{(4J^*-15)}{4\sqrt{35}}(6+3\sqrt{10}) + \frac{3}{5\sqrt{6}}(4J^*-33)$	$-\frac{3(4J^*-15)}{14\sqrt{5}} + \sqrt{\frac{18}{14}} - \frac{3}{7\sqrt{22}}(4J^*-57)$	$-\frac{6(1+\sqrt{3})}{\sqrt{21}}$	$\frac{6}{\sqrt{154}}$

for simplicity, only the second-order perturbation effect of the spin-orbit interaction on the ground orbital singlet (denoted by 0 below). Other higher-order perturbation contributions are dealt with explicitly elsewhere. Integrating over the orbital variables one obtains [24]

$$E^{(2)} = \lambda^2 \sum_n \frac{(\mathbf{L}_{0n} \cdot \mathbf{S})(\mathbf{L}_{n0} \cdot \mathbf{S})}{E_0 - E_n} \quad (36)$$

where  $L_{0n}$  denotes the matrix element  $\langle 0 | L | n \rangle \equiv L_{0n}^{(1)}$  with 0 and  $n$  referring to the ground and excited states, respectively, and  $E_i$  denotes energy. Using (34) we immediately obtain the ZFS term in the spin Hamiltonian as

$$\mathcal{H}_s = \sum_{kq} B_q^{(k)} O_q^{(k)}(S) \quad (37)$$

where

$$B_q^{(k)} = \lambda^2 \varepsilon_k^{(1,1)} (-1)^{k-q} \sum_n \frac{[\mathbf{L}_{0n}^{(1)} \times \mathbf{L}_{n0}^{(1)}]_{-q}^{(k)}}{E_0 - E_n} \quad (38)$$

The values of  $\varepsilon_k^{(1,1)}$  can be found in table 1.

Using (36), the conventional derivation of the spin Hamiltonian [9] yields only the form  $\mathcal{H}_s = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$ . The conventional derivation is not suitable for derivation of the higher-order perturbation contributions as it cannot handle the spin-spin interaction. Thus the spin-Hamiltonian derivation by the tensor algebra outlined above provides means of taking into account fully any interaction expressed in terms of tensor operators. For instance, the spin-spin interaction (35) produces the second-order contribution to the spin-Hamiltonian parameter  $B_q^{(k)}$  in (37) given by

$$B_q^{(k)} = \frac{4}{9} \rho^2 \varepsilon_k^{(2,2)} (-1)^{k-q} \sum_n \frac{[\mathbf{L}_{0n}^{(2)} \times \mathbf{L}_{n0}^{(2)}]_{-q}^{(k)}}{E_0 - E_n} \quad (39)$$

where  $L_{0n}^{(2)} \equiv \langle 0 | O^{(2)}(L) | n \rangle$ . Values of  $\varepsilon_k^{(2,2)}$  can be found in table 1. The tensor method of derivation of the spin Hamiltonian will be used for the consideration of the pseudo-quadrupole interaction in NMR spectroscopy [13] in a future paper.

## 6. Conclusions

Irreducible products of irreducible tensor operators  $O^{(k_2)}(J)$  obeying special commutation relations arising from the properties of angular momentum operators can be expressed in terms of  $O^{(k)}$  associated with a coupling coefficient  $\varepsilon_k^{(k_1, k_2)}$ . The symmetry properties of this coefficient reveal the equality  $[O^{(k_1)} \times O^{(k_2)}]^{(k)} = [O^{(k_2)} \times O^{(k_1)}]^{(k)}$ . This result differs from the corresponding result for the coupling of commuting tensor operators. Multiple products have also been discussed. An analytical expression has been derived for the coupling coefficient  $\varepsilon_k^{(k_1, k_2)}$  and used to tabulate its values for several important cases. The present considerations reveal several symmetry properties of the coupling coefficients for multiple irreducible products of tensorial sets. The numerical results are useful in the study of higher-order effects in spectroscopy.

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