Journal of Magnetic Resonance **140,** 141–145 (1999)
Article ID jmre.1999.1783, available online at http://www.idealibrary.com on IDEAL®

On the Generation of Operator Equivalents and the Calculation of Their Matrix Elements

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Received November 24, 1998; revised March 31, 1999

To find all components $T^{(k)}_{\pm q} = N_{k,q}J^q_\pm \sum_{m=0}^{k-q} (\pm 1)^{k-m}a(k, q; m)J^m_z$ $(0 \le q \le k)$ of an irreducible tensor operator of rank k, a recursion formula for the coefficients $a(k, q; m)$ is derived. Various kinds of operator equivalents and forms of their expression are examined. Matrix elements of operator equivalents are expressed through the coefficients $a(k, q; m)$. A table for the coefficients $a(k, q; m)$ with $k = 2$, 4, and 6 is given. © 1999 Academic Press

Key Words: **tensor operators; operator equivalents; matrix elements.**

INTRODUCTION

Operator equivalents play a fundamental role in magnetic resonance (EPR, ENDOR, etc.), especially in the construction of a symmetry-adapted spin Hamiltonian followed by the calculation of the energy levels of paramagnetic ions in crystals. Both Stevens operator equivalents and Racah operator equivalents are extensively used for this purpose (see, e.g., (*1*, *2*) and (*3*, *4*), respectively, and references therein). Actually the latter are the components (denoted here as $T^{(k)}_{\pm q}$) of the irreducible tensor operator (*5*) $\mathbf{T}^{(k)}(\mathbf{J})$ of an angular momentum $\mathbf{J} = (J_x, J_y, J_z)$ and the former are linear combinations of the operators $T^{(k)}_q$ and $T^{(k)}_{-q}$ (see, e.g., (*6*) and the summary therein of the different notations for operator equivalents).

Until now several methods for generating operator equivalents have been known. The best known originated from Stevens (*7*) and consists in replacing the space variables x, y, and z, which appear in expressions for solid (spherical or tesseral) harmonics, with the operators J_x, J_y, and J_z, respectively. Conversion from solid harmonics to operator equivalents can also be carried out by the "polarization" process (*8*). Another way is to apply Racah's (*5*) commutation rule (see Eq. [1] below). Direct use of the above methods is complicated with an increase of order k by noncommutation of the operators J_x, J_y, and J_z. In solving the problem of generating operator equivalents of high order some general formula or an elaborated algorithm might be very useful. The available formulas (*9–11*) and algorithms (*3*, *4*) seem to be much too complicated for application in practice. One of the purposes of the present work is to give much simpler formulas for constructing operator equivalents as well as calculating their matrix elements. Another purpose is to inspect various kinds of operator equivalents as well as forms of their expression.

GENERATION OF TENSOR OPERATORS $\mathbf{T}^{(k)}(\mathbf{J})$

The components $T^{(k)}_{\pm q}$ of an irreducible tensor operator $\mathbf{T}^{(k)}(\mathbf{J})$ of order k $(0 \le q \le k)$ satisfy Racah's commutation rule (*5*):

$$[J_\mp, T^{(k)}_{\pm q}] = [(k+q)(k-q+1)]^{1/2}T^{(k)}_{\pm q \mp 1}. \qquad [1]$$

The "$\pm q$" and "$\mp q$" components are related to one another by (*5*)

$$T^{(k)\dagger}_{\pm q} = (-1)^q T^{(k)}_{\mp q}. \qquad [2]$$

Starting from the "$\pm k$" component $T^{(k)}_{\pm k} = N_{k,\pm k}J^k_\pm$ and using Eq. [1] along with the standard commutation relations for the components $J_\pm = J_x \pm iJ_y$ and J_z of an angular momentum $\mathbf{J}$ (see, e.g., (*12*)), we obtain

$$T^{(k)}_{\pm q} = N_{k,\pm q}J^q_\pm \sum_{m=0}^{k-q} a(k, \pm q; m)J^m_z, \qquad [3]$$

where

$$N_{k,q} = (-1)^{k-q}N_{k,k}\left[\frac{(k+q)!}{(k-q)!(2k)!}\right]^{1/2}, \qquad [4]$$

$$N_{k,-q} = (-1)^k N_{k,q}, \qquad [5]$$

$N_{k,k}$ is a normalization factor (see the next paragraph), and

$$a(k, -q; m) = (-1)^m a(k, q; m). \qquad [6]$$

Equations [3], [5], and [6] result in

$$T^{(k)}_{\pm q} = N_{k,q}J^q_\pm \sum_{m=0}^{k-q} (\pm 1)^{k-m}a(k, q; m)J^m_z. \qquad [7]$$

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All coefficients $a(k, q; m)$ are not equal to zero only if $q + m \leq k$; in particular when $q = k$ they are $a(k, k; 0) = 1$. The "$q - 1$" coefficients are related to the "q" coefficients by a recursion formula:

$$a(k, q-1; m) = (2q + m - 1)a(k, q; m-1) + \left[q(q-1) - \frac{m(m+1)}{2}\right]a(k, q; m) + \sum_{n=1}^{k-q-m} (-1)^n \left[\binom{m+n}{m} J(J+1) - \binom{m+n}{m-1} - \binom{m+n}{m-2}\right] \times a(k, q; m+n). \quad [8]$$

In addition,

$$N_{k,q-1} = -\frac{N_{k,q}}{[(k+q)(k-q+1)]^{1/2}}. \quad [9]$$

The coefficients $a(k, q; m)$ can be considered as

$$a(k, q; m) = \sum_{i=0}^{[(k-q-m)/2]} [J(J+1)]^i a(k, q; m, i), \quad [10]$$

where the fourth index i is an integer power of the eigenvalue of $\mathbf{J}^2$, the maximum for i being the integer part of the number $(k - q - m)/2$. The algorithm, given in Eq. [8], is easily programmed on a computer with the result that all components (see Eq. [7]) of the tensor operator $\mathbf{T}^{(k)}(\mathbf{J})$ of order as high as, e.g., 50 can be found. As an illustration, all coefficients except for $N_{k,k}$ appropriate to the most common magnetic resonance orders, $k = 2$, 4, and 6, are given in Table 1. The specific values of $N_{k,k}$ are determined by a concrete kind of tensor operator (see below).

KINDS OF OPERATOR EQUIVALENTS

The operators $T^{(k)}_{\pm q}$ defined in Eq. [7] are the direct equivalents of solid harmonics

$$r^k C^{(k)}_{\pm q} \equiv r^k \left(\frac{4\pi}{2k+1}\right)^{1/2} Y^{(k)}_{\pm q}, \quad [11]$$

where $Y^{(k)}_{\pm q}$ are the usual spherical harmonics and $C^{(k)}_{\pm q}$ are Racah's harmonics (*5*), if we put in Eq. [4]

$$N_{k,k} = \frac{(-1)^k[(2k)!]^{1/2}}{2^k k!}. \quad [12]$$

TABLE 1
The Coefficients Appropriate to the Racah and Stevens Operator Equivalents Defined in Eqs. [7] and [23] with $k = 2$, 4, and 6

k	q	$N_{k,q}/N_{k,k}$	m	$a(k, q; m)/F_{k,q}$	$F_{k,q}$
2	0	$6^{-1/2}/2$	0	$-X$	4
			2	3	
	1	$-\frac{1}{2}$	0	1	2
			1	2	
	2	1	0	1	1
4	0	$70^{-1/2}/24$	0	$-3X(2 - X)$	48
			2	$5(5 - 6X)$	
			4	35	
	1	$-14^{-1/2}/12$	0	$3(2 - X)$	24
			1	$19 - 6X$	
			2	21	
			3	14	
	2	$7^{-1/2}/4$	0	$9 - X$	8
			1	14	
			2	7	
	3	$-2^{-1/2}/2$	0	3	4
			1	2	
	4	1	0	1	1
6	0	$231^{-1/2}/1440$	0	$-5X(12 - 8X + X^2)$	2880
			2	$21(14 - 25X + 5X^2)$	
			4	$105(7 - 3X)$	
			6	231	
	1	$-22^{-1/2}/720$	0	$5(12 - 8X + X^2)$	1440
			1	$2(117 - 55X + 5X^2)$	
			2	$15(25 - 6X)$	
			3	$60(6 - X)$	
			4	165	
			5	66	
	2	$55^{-1/2}/72$	0	$120 - 26X + X^2$	360
			1	$6(47 - 6X)$	
			2	$3(91 - 6X)$	
			3	132	
			4	33	
	3	$-55^{-1/2}/12$	0	$3(40 - 3X)$	60
			1	$179 - 6X$	
			2	99	
			3	22	
	4	$66^{-1/2}/2$	0	$50 - X$	12
			1	44	
			2	11	
	5	$-3^{-1/2}/2$	0	5	6
			1	2	
	6	1	0	1	1

Note. $X = J(J + 1)$; $F_{k,q}$ are multiplying factors.

The operator equivalents with such normalization are traditionally expressed (see, e.g., (*4, 13–15*)) through anti-commutators $\{J^q_\pm, P^{k-q}(J_z)\} \equiv J^q_\pm P^{k-q} + P^{k-q} J^q_\pm$, i.e.,

$$T^{(k)}_{\pm q} = (\pm 1)^q N_{k,q} \{J^q_\pm, P^{k-q}(J_z)\}, \quad [13]$$

where we introduce the designation $P^{k-q}(J_z)$ for a polynomial of order $k - q$ in the variable J_z having orders $k - q$, $k - q -$

$2, \ldots \geq 0$. We found that each pair of those operators can also be expressed as the sum/difference of another anti-commutator $\{J^q_\pm, P'^{k-q}(J_z)\} \neq \{J^q_\pm, P^{k-q}(J_z)\}$ and commutator $[J^q_\pm, P^{k-q-1}(J_z)] \equiv J^q_\pm P^{k-q-1} - P^{k-q-1}J^q_\pm$,

$$T^{(k)}_{\pm q} = (\pm 1)^q N_{k,q}(\{J^q_\pm, P'^{k-q}(J_z)\} \pm [J^q_\pm, P^{k-q-1}(J_z)]), \quad [14]$$

where in a polynomial of order $k - q - 1$ the variable J_z has orders $k - q - 1, k - q - 3, \ldots > 0$. In addition, for $q \neq 0$ the alternative form is

$$T^{(k)}_{\pm q} = (\pm 1)^{q+1} N_{k,q}[J^q_\pm, P^{k-q+1}(J_z)]; \quad [15]$$

here orders of J_z are $k - q + 1, k - q - 1, \ldots > 0$. All these forms, Eqs. [13]–[15], can be reduced to Eq. [7] with the help of the relation

$$J^p_z J^q_\pm = J^q_\pm (J_z \pm q)^p = J^q_\pm \sum_{m=0}^{p} (\pm 1)^m \binom{p}{m} q^m J^{p-m}_z. \quad [16]$$

For example, for the component $T^{(6)}_{\pm 1}$ Eqs. [13]–[15] give

$$T^{(6)}_{\pm 1} = \pm N_{6,1}F_{6,1}\{J_\pm, 33J^5_z - (30X - 15)J^3_z + (5X^2 - 10X + 12)J_z\}, \quad [13']$$

$$T^{(6)}_{\pm 1} = N_{6,1}F_{6,1}\left(\pm\left\{J_\pm, 33J^5_z - (30X - 75)J^3_z + \left(5X^2 - \frac{35}{2}X + 12\right)J_z\right\} + \left[J_\pm, 30J^4_z - \left(\frac{15}{2}X - 30\right)J^2_z\right]\right), \quad [14']$$

$$T^{(6)}_{\pm 1} = N_{6,1}F_{6,1}[J_\pm, -11J^6_z + (15X - 35)J^4_z - (5X^2 - 25X + 14)J^2_z], \quad [15']$$

where $F_{6,1} = 1440$ and $X = J(J + 1)$. But all these are reduced to the following (cf. Table 1):

$$T^{(6)}_{\pm 1} = N_{6,1}F_{6,1}J_\pm[\pm 66J^5_z + 165J^4_z \pm 60(-X + 6)J^3_z + 15(-6X + 25)J^2_z \pm 2(5X^2 - 55X + 117)J_z + 5(X^2 - 8X + 12)]. \quad [7']$$

Introducing

$$N_{k,k} = \frac{(-1)^k}{2^{k/2}} \quad [17]$$

in Eq. [4], we obtain from Eq. [7] the operator equivalents (see Ref. (*3*)) commonly used in constructing a generalized spin Hamiltonian (*16*).

In the case

$$N_{k,k} = \frac{(-1)^k}{k!}\left[\frac{(2k)!(2J - k)!}{(2J + k + 1)!}\right]^{1/2} \quad [18]$$

we get Racah's (*5*) unit tensor operators, for which the reduced matrix elements are

$$\langle J \| T^{(k)} \| J \rangle = 1. \quad [19]$$

This result (cf. Eq. [29] below) follows from the Wigner–Eckart theorem (*17*) (see Eq. [28]). The normalization, which is similar to Eq. [18] but includes an additional factor $(2k + 1)^{1/2}$, gives (*18*)

$$\langle J \| T^{(k)} \| J \rangle = (2k + 1)^{1/2}. \quad [20]$$

The normalization $N_{k,k} = 1$ (*12*) and others (see, e.g., the normalization of the operators $T^{(2)}_{\pm q}$ in Ref. (*19*)) are also used.

The operator equivalents to the cosine and sine tesseral harmonics are linear combinations of the appropriate tensor operators of a spherical type, viz.,

$$O^q_k(c) = \frac{c_{k,q}}{2}[T^{(k)}_q + T^{(k)\dagger}_q],$$

$$O^q_k(s) = \frac{c_{k,q}}{2i}[T^{(k)}_q - T^{(k)\dagger}_q], \quad [21]$$

where $c_{k,q}$ is a multiplying coefficient. In particular, the conventional Stevens operator equivalents are obtained with the use of

$$c_{k,q} = \frac{\alpha}{N_{k,q}F_{k,q}}, \quad [22]$$

where $F_{k,q}$ is the largest common factor for the natural numbers $a(k, q; m, i)$ (see Eq. [10]) with given k and q (see the values of $F_{k,q}$ for $k = 2$, 4, and 6 in Table 1); $\alpha = 1$ for all q if k is an odd integer but if k is even, then $\alpha = 1$ or $\alpha = \frac{1}{2}$ for even and odd q, respectively. Thus, for the conventional Stevens operator equivalents from Eqs. [2], [7], [21], and [22] we get

$$O^q_k(c) \equiv O^q_k = \frac{\alpha}{2F_{k,q}} \sum_{m=0}^{k-q} a(k, q; m) \times [J^q_+ + (-1)^{k-q-m} J^q_-]J^m_z,$$

$$O^q_k(s) = \frac{\alpha}{2iF_{k,q}} \sum_{m=0}^{k-q} a(k, q; m) \times [J^q_+ - (-1)^{k-q-m} J^q_-]J^m_z. \quad [23]$$

The above-stated double value α can apparently be explained as follows. When constructing the operators $O_k^q(c)$ and $O_k^q(s)$ with Eq. [21] the tensor operators $T_{\pm q}^{(k)}$ are usually used in a form similar to Eq. [13]. Then for the Stevens operators with even k the common factors $F'_{k,q} = F_{k,q}/\alpha$ appear in polynomials $P^{k-q}(J_z)$, i.e.,

$$O_k^q = \frac{1}{2F'_{k,q}} \{J_+^q + J_-^q, P^{k-q}(J_z)\}, \qquad [24]$$

each factor $F'_{k,q}$ being just the same that would appear in constructing the solid harmonics (see Eq. [11]). In the case of odd k the multiplying factors $F'_{k,q} = F_{k,q}$ are conventionally chosen as the common ones for the corresponding polynomials in the solid harmonics rather than for the polynomials $P^{k-q}(J_z)$. As a consequence of this trick fractional numbers occur in the appropriate anti-commutators (see, e.g., the lists of Racah and Stevens operator equivalents in Refs. (*14, 15*) and (*2, 21*), respectively; the list in Ref. (*21*), however, is found to contain a number of errors). By the way, following Ref. (*11*), we note that terms of order lower than k in Eq. [7] (bearing in mind orders in Eq. [10]) are to be ignored when performing the reciprocal conversion from the operator equivalents to the solid harmonics. From the above it can be concluded that in the construction of the Hermitian operators $O_k^q(c)$ and $O_k^q(s)$ other values of the coefficients $c_{k,q}$ in Eq. [21] would be desirable in order to exclude any dependence on the form of expression of the tensor operators $T_{\pm q}^{(k)}$. The value $c_{k,q} = 1$ seems to be quite suitable.

MATRIX ELEMENTS OF OPERATOR EQUIVALENTS

Knowing that

$$J_z|J, M\rangle = M|J, M\rangle$$

and

$$J_\pm|J, M\rangle = [(J \mp M)(J \pm M + 1)]^{1/2}|J, M \pm 1\rangle, \qquad [25]$$

we get from Eq. [7]

$$\langle J, M \pm q|T_{\pm q}^{(k)}|J, M\rangle = N_{k,q}\left[\frac{(J \mp M)!(J \pm M + q)!}{(J \pm M)!(J \mp M - q)!}\right]^{1/2} \times \sum_{m=0}^{k-q} (\pm 1)^{k-m} M^m a(k, q; m) \qquad [26]$$

with the restrictions $0 \le q \le k \le 2J$ and $-J \le M \pm q \le J$. For example, using Eqs. [4] and [26] as well as Table 1, tables (see Ref. (*20*)) of matrix elements of Racah operator equivalents with normalization from Eq. [12] can be easily reproduced for $k = 2$, 4, and 6. For the practically important Stevens operator equivalents, Eqs. [23], we analogously obtain

$$\langle J, M'|O_k^q(c)|J, M\rangle = \frac{\alpha}{2F_{k,q}} \sum_{m=0}^{k-q} \times \left\{ \delta_{M',M+q}\left[\frac{(J-M)!(J+M+q)!}{(J+M)!(J-M-q)!}\right]^{1/2} + \delta_{M',M-q}(-1)^{k-q-m}\left[\frac{(J+M)!(J-M+q)!}{(J-M)!(J+M-q)!}\right]^{1/2}\right\} \times M^m a(k, q; m) \qquad [27]$$

and a similar formula for $O_k^q(s)$, in which an additional multiplier $(-i)$ is to appear and the sign in front of $(-1)^{k-q-m}$ is to be changed into the opposite. With Eq. [27] some misprints in the available tables of matrix elements of Stevens operator equivalents (see, e.g., the Russian edition of books (*1, 2*)) can come to light.

According to the Wigner–Eckart theorem (*17*), matrix elements of irreducible tensor operators $\mathbf{T}^{(k)}(\mathbf{J})$ are

$$\langle J, M \pm q|T_{\pm q}^{(k)}|J, M\rangle = (-1)^{J-M\mp q}\begin{pmatrix} J & k & J \\ -M \mp q & \pm q & M \end{pmatrix}\langle J\|T^{(k)}\|J\rangle. \qquad [28]$$

Putting $q = k$ and comparing the right-hand sides in Eqs. [26] and [28], we get

$$\langle J\|T^{(k)}\|J\rangle = (-1)^k N_{k,k} k!\left[\frac{(2J+k+1)!}{(2k)!(2J-k)!}\right]^{1/2}. \qquad [29]$$

The special cases of Eq. [29] appropriate to the normalizations in Eqs. [12], [17], and [18] have been considered in Refs. (*14, 15*), (*3*), and (*11*), respectively.

CONCLUSIONS

The new formulas given in this work, viz., Eqs. [4], [7]–[10], [23], [26], and [27], constitute the closed and easily reproduced algorithm of constructing quickly both the Racah and the Stevens operator equivalents ($T_{\pm q}^{(k)}$ and $O_k^q(c)$, $O_k^q(s)$) with any (reasonably high) integer order k and any normalization, such as in Eqs. [12], [17], [18], or any other, as well as of calculating their matrix elements (within any J = constant) without any reference to the special tables. The available tables quite often contain annoying misprints and our formulas could be useful in revealing these.

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