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Generalization of Stevens' operator-equivalent method

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Abstract. The operator-equivalent method was introduced by Stevens in 1952. This method enabled him to determine the quantum mechanical equivalent of a given spherical harmonic C_{kq}—the so-called Racah tensor operator $\hat{C}_{kq}$—as an explicit function of the total angular momentum operator $\hat{J}$ within a constant J manifold. The method itself uses spherical harmonics in cartesian coordinates and from each spherical harmonic the corresponding Racah tensor operator is calculated. This paper shows that it is useful to fix $\tau := k - |q|$ as all spherical harmonics $C_{|q|+\tau,|q|}$ possess the same polynomial structure with coefficients showing a simple dependence on the absolute value of q. For the following Racah operators $\hat{C}_{|q|+\tau,|q|}$, which hold for all $|q|$, Stevens' operator-equivalent method has to be generalized. By an application of the Wigner–Eckart theorem to the operator-equivalents $\hat{C}_{|q|+\tau,|q|}(J)$, the $3j$-symbols with two identical js disclose its innermost functional dependence on the variables. To give an example the calculations are explicitly stated for $\tau = 0, 1, 2, \ldots, 5$.

1. Introduction

Between 1942 and 1949 Racah published four papers [2–5] under the general title 'Theory of Complex Spectra'. Before the publication of these papers certain rules were used—formulated by Slater [6] in 1929—to determine the energy levels of electrons in complex atoms. With the introduction of tensor operators Racah could prove these rules, while a further application of Lie's theory of continuous groups led him to a classification of configurations of equivalent f electrons. According to Racah a tensor operator $\hat{C}_{kq}$ and a spherical harmonic C_{kq} transform identically under any rotation of the total angular momentum operator $\hat{J}$. As the transformation properties are completely determined by the commutator relations with $\hat{J}$, a tensor operator satisfies:

$$\begin{aligned} \left[\hat{J}_z, \hat{C}_{kq}\right] &= q\hat{C}_{kq} \\ \left[\hat{J}_\pm, \hat{C}_{kq}\right] &= \sqrt{k(k+1) - q(q\pm 1)}\hat{C}_{k,q\pm 1}. \end{aligned} \tag{1}$$

Stevens' operator-equivalent method is based on the coincidence of the commutator relations of tensor operators and spherical harmonics: if $\hat{J}$ is fixed to a certain value J, the step of quantization from a spherical harmonic to a tensor operator is given by a change of representation of the spherical harmonics:

$$C_{kq}\left(\frac{\boldsymbol{r}}{|\boldsymbol{r}|}\right) \overset{\text{quantization}}{\longrightarrow} C_{kq}(\hat{\boldsymbol{J}}) = \hat{C}_{kq}(\boldsymbol{J}). \tag{2}$$

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Attention has to be paid to the fact that the components of the angular momentum operator $\hat{\boldsymbol{J}}$ do not commute. Thus, the spherical harmonics first have to be transformed in a system of cartesian coordinates—the commutator relations among the components of $\hat{\boldsymbol{J}}$ are only known in such systems—while after substituting $\boldsymbol{r}/|\boldsymbol{r}|$ by $\hat{\boldsymbol{J}}$, each term in a sum has to be made symmetric in $\hat{\boldsymbol{J}}_x$, $\hat{\boldsymbol{J}}_y$ and $\hat{\boldsymbol{J}}_z$. Of course, the calculation of these symmetrizations are in general very tedious. Fortunately—as we will see later—all symmetrizations can be simplified and then determined by a computer program.

One degree of freedom is left by (1): $\theta\hat{C}_{kq}$ is, like $\hat{C}_{kq}$, a tensor operator of rank k as long as the constant θ is independent of q. For the so-called operator-equivalent $\hat{C}_{kq}(\boldsymbol{J})$ and the Racah operator $\hat{C}_{kq}$ it is generally used:

$$\hat{C}_{kq} = \theta_k \hat{C}_{kq}(\boldsymbol{J}). \tag{3}$$

In the theory of crystal fields the operator-equivalent factors θ_2, θ_4, θ_6 are well known as the Stevens' factors α_J, β_J, and γ_J. An application of the Wigner–Eckart theorem to (3) for a system of n equivalent electrons, each with orbital momentum l and forming eigenstates $^{2S+1}L_J$, leads to the expression [7, 8]:

$$\begin{aligned}\theta_k(l^n, {}^{2S+1}L_J) &= (2l+1)(2J+1)2^k\sqrt{\frac{(2J-k)!}{(2J+k+1)!}}(-1)^{S+L+J+l} \\ &\times \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} J & k & J \\ L & S & L \end{Bmatrix} \langle l^{n\,2S+1}L\|\hat{E}_k\|^{2S+1}Ll^n\rangle.\end{aligned} \tag{4}$$

The reduced matrix elements of the unit tensor operator $\hat{E}_{kq}$ are tabulated for all p^n, d^n and f^n configurations by Nielson and Koster [9], while the $3j$- and $6j$-symbols can be found in Rotenberg [10]. Due to certain selection rules of the $3j$- and $6j$-symbols the constant θ_k is only non-vanishing for few values of k:

$$k = \begin{cases} 0, 2, 4, \ldots, \min\{2J, 2l\} & \text{if } 2J \text{ is even} \\ 0, 2, 4, \ldots, \min\{2J-1, 2l\} & \text{if } 2J \text{ is odd.} \end{cases} \tag{5}$$

2. The spherical harmonics in cartesian coordinates

To transform the spherical harmonics into a system of cartesian coordinates, we use a definition given by Judd [11]:

$$C_{k,|q|}(\theta, \phi) = \sqrt{\frac{(k-|q|)!}{(k+|q|)!}} P_k^{|q|}(\cos\theta)\mathrm{e}^{\mathrm{i}q\phi} \tag{6}$$

with $k = 0, 1, 2, \ldots$ and $|q| \leq k$. The transformation properties of spherical harmonics with negative values of q can be found by complex conjugation and multiplication by $(-1)^{|q|}$ of (6). If we use the definition of the Legendre functions $P_k^q(x)$:

$$P_k^q(x) = \frac{(-1)^q}{2^k k!}(1-x^2)^{q/2}\frac{\mathrm{d}^{k+q}}{\mathrm{d}x^{k+q}}(x^2-1)^k \tag{7}$$

we find by straightforward calculation an equation which expresses the spherical harmonics in cartesian coordinates:

$$r^k C_{k,|q|}(\theta,\phi) = \beta_{k,|q|}(x+\mathrm{i}y)^{|q|} G_{k,|q|}(r,z) \tag{8}$$

where $r^2 = x^2 + y^2 + z^2$. The constant $\beta_{k,|q|}$ and the polynomial function $G_{k,|q|}(r,z)$ are defined by:

$$\beta_{k,|q|} := \frac{k!}{2^k} \frac{(-1)^{|q|}}{\sqrt{(k-|q|)!(k+|q|)!}} \tag{9}$$

$$G_{k,|q|}(r,z) := \sum_{j=0}^{k-|q|} \binom{|q|+k}{|q|+j} \binom{k-|q|}{j} (z+r)^j (z-r)^{k-|q|-j}. \tag{10}$$

In table 1 the $G_{k,|q|}(r,z)$ are listed for $k = 0, 1, \ldots, 5$. This table provides the idea to order the polynomials $G_{k,|q|}$ by $\tau := k - |q|$ as those functions seem to have the same polynomial structure in z and r. To see this from (10), we define $n := |q|$ and the coefficients in $G_{k,|q|}$ by:

$$a_{n\tau j} := \binom{2n+\tau}{n+j} \binom{\tau}{j}. \tag{11}$$

Table 1. The polynomial functions $G_{k,|q|}(r,z)$ for $k = 0, 1, \ldots, 5$.

$G_{00} = 1$
$G_{10} = 2z$
$G_{11} = 2$
$G_{20} = 6z^2 - 2r^2$
$G_{21} = 6z$
$G_{22} = 6$
$G_{30} = 20z^3 - 12zr^2$
$G_{31} = 20z^2 - 4r^2$
$G_{32} = 20z$
$G_{33} = 20$
$G_{40} = 70z^4 - 60z^2r^2 + 6r^4$
$G_{41} = 70z^3 - 30zr^2$
$G_{42} = 70z^2 - 10r^2$
$G_{43} = 70z$
$G_{44} = 70$
$G_{50} = 252z^5 - 280z^3r^2 + 60zr^4$
$G_{51} = 252z^4 - 168z^2r^2 + 12r^4$
$G_{52} = 252z^3 - 84zr^2$
$G_{53} = 252z^2 - 28r^2$
$G_{54} = 252z$
$G_{55} = 252$

For all coefficients $a_{n\tau j}$ the equation: $a_{n\tau,\tau-j} = a_{n\tau j}$ holds, and (10) is rewritten more skilfully to:

$$G_{n+\tau,n}(r,z) = \frac{1}{2}\sum_{j=0}^{\tau} a_{n\tau j}\left[(z+r)^j(z-r)^{\tau-j} + (z+r)^{\tau-j}(z-r)^j\right]. \tag{12}$$

On the other hand we have for the term enclosed by the rectangular brackets:

$$(z+r)^j(z-r)^{\tau-j} + (z+r)^{\tau-j}(z-r)^j = 2\sum_{\substack{v=0\\ v \text{ even}}}^{\tau} b_{j\tau v} z^{\tau-v} r^v \tag{13}$$

with the integers $b_{j\tau v}$:

$$b_{j\tau v} := \sum_{0\le p=v+j-\tau\le v}^{j} (-1)^p \binom{j}{p}\binom{\tau-j}{v-p}. \tag{14}$$

The left-hand side of (13) is invariant under a substitution $\tau - j$ for j. Thus, for the $b_{j\tau v}$ the equation: $b_{\tau-j,\tau v} = b_{j\tau v}$ holds. Finally, if we replace (13) and (14) in (12), $G_{n+\tau,n}$ looks like:

$$G_{n+\tau,n}(r^2,z) = \sum_{\substack{v=0\\ v \text{ even}}}^{\tau} g_{n\tau v} z^{\tau-v} r^v \tag{15}$$

with the integer coefficients $g_{n\tau v}$:

$$g_{n\tau v} := \sum_{j=0}^{\tau} a_{n\tau j} b_{j\tau v}. \tag{16}$$

Three properties of the functions $G_{n+\tau,n}(r^2,z)$ should be pointed out here. First, the $G_{n+\tau,n}$ are even functions of r. This ensures that the operator-equivalents $\hat{C}_{n+\tau,n}(\boldsymbol{J})$ are only functions of $\hat{\boldsymbol{J}}^2$, $\hat{\boldsymbol{J}}_z$ and $\hat{\boldsymbol{J}}_+$. Second, as r^2 is equal to $(x^2+y^2+z^2)$, the polynomial functions $G_{n+\tau,n}$ are of degree τ in the three components of $\boldsymbol{r}$. Third, the functions $G_{n+\tau,n}$ with fixed τ and n can be divided by a rational number which is in general different from one. To determine the so-called greatest common divisor $\mathrm{gcd}_{n+\tau,n}$, we point out that $g_{n\tau 0}$, the coefficient of z^τ in $G_{n+\tau,n}$, can be easily calculated:

$$g_{n\tau 0} = \sum_{j=0}^{\tau}\binom{2n+\tau}{n+j}\binom{\tau}{j} = \frac{[2(n+\tau)]!}{(n+\tau)!^2}. \tag{17}$$

If we introduce polynomial functions $H_{n+\tau,n}$ by $G_{n+\tau,n}/\mathrm{gcd}_{n+\tau,n}$ and the constants $\epsilon_{n+\tau,n}$ by $\beta_{n+\tau,n}\mathrm{gcd}_{n+\tau,n}$ and denote the coefficients of $H_{n+\tau,n}$ by $h_{n\tau v}$, we can define

$$\mathrm{gcd}_{n+\tau,n} := \frac{[2(n+\tau)]!}{(n+\tau)!^2}\frac{1}{h_{n\tau 0}} \tag{18}$$

where $h_{n\tau 0}$ is the coefficient of z^τ in $H_{n+\tau,n}$. An application of equations (11), (14), (15), (16) and (18) yields for the first six functions $H_{n+\tau,n}$:

$$\begin{aligned}
H_{n+0,n} &= 1 \\
H_{n+1,n} &= z \\
H_{n+2,n} &= (2n+3)z^2 - r^2 \\
H_{n+3,n} &= (2n+5)z^3 - 3zr^2 \\
H_{n+4,n} &= (2n+5)(2n+7)z^4 - 6(2n+5)z^2r^2 + 3r^4 \\
H_{n+5,n} &= (2n+7)(2n+9)z^5 - 10(2n+7)z^3r^2 + 15zr^4.
\end{aligned} \tag{19}$$

For later reference we define polynomial functions $P_{n+\tau,n}(x,y,z)$ including the whole r-dependence:

$$P_{n+\tau,n}(x,y,z) := (x+\mathrm{i}y)^n H_{n+\tau,n}(r^2,z) \tag{20}$$

using the already mentioned functions $H_{n+\tau,n}(r^2,z)$:

$$H_{n+\tau,n}(r^2,z) = \sum_{\substack{v=0 \\ v\ \text{even}}}^{\tau} h_{n\tau v} z^{\tau-v} r^v. \tag{21}$$

Equation (8) can be rewritten to:

$$r^{n+\tau} C_{n+\tau,n}(\theta,\phi) = \epsilon_{n+\tau,n} P_{n+\tau,n}(x,y,z) \tag{22}$$

with the constants $\epsilon_{n+\tau,n}$:

$$\epsilon_{n+\tau,n} = \frac{1}{2^{n+\tau}} \frac{[2(n+\tau)]!}{(n+\tau)!} \frac{(-1)^n}{\sqrt{\tau!(2n+\tau)!}} \frac{1}{h_{n\tau 0}}. \tag{23}$$

3. Calculation of the operator-equivalents $\hat{C}_{n+\tau,n}(J)$ with τ fixed but n arbitrary

To determine the operator-equivalents $\hat{C}_{n+\tau,n}(J)$, we first replace in $H_{n+\tau,n}$ the vth power of r by $(x^2+y^2+z^2)^{v/2}$ namely for all even numbers v between 0 and τ. Each term of $P_{n+\tau,n}$ is therefore of the form

$$(x+\mathrm{i}y)^n x^p y^{t-p} z^{\tau-t} \tag{24}$$

with t even, also lying between 0 and τ, and with p even, lying between 0 and t. A first formula for the operator-equivalents can be given, if we apply the operator-equivalent method defined by (2) to (22):

$$\hat{C}_{n+\tau,n}(J) = \epsilon_{n+\tau,n} \hat{P}_{n+\tau,n}(J). \tag{25}$$

According to (24) and (22) each term of $\hat{P}_{n+\tau,n}(\boldsymbol{J})$ transforms to:

$$\left\{(\hat{\boldsymbol{J}}_x + \mathrm{i}\hat{\boldsymbol{J}}_y)^n \hat{\boldsymbol{J}}_x^p \hat{\boldsymbol{J}}_y^{t-p} \hat{\boldsymbol{J}}_z^{\tau-t}\right\}^{\hat{\boldsymbol{J}}_x, \hat{\boldsymbol{J}}_y, \hat{\boldsymbol{J}}_z} . \tag{26}$$

The curly brackets denote that the enclosed term has to be made symmetric with regard to any permutation of operators shown by the right superscript. The operator-equivalent method therefore specifies $n+1$ symmetrizations for each term of $P_{n+\tau,n}(\boldsymbol{J})$. Fortunately, we may simplify these to only one per term by introducing additionally the raising operator $\hat{\boldsymbol{J}}_+$:

$$\left\{\hat{\boldsymbol{J}}_+^n \hat{\boldsymbol{J}}_x^p \hat{\boldsymbol{J}}_y^{t-p} \hat{\boldsymbol{J}}_z^{\tau-t}\right\}^{\hat{\boldsymbol{J}}_+, \hat{\boldsymbol{J}}_x, \hat{\boldsymbol{J}}_y, \hat{\boldsymbol{J}}_z} . \tag{27}$$

Using the method of recursive symmetrization, which will be presented later in the text, this simplification is straightforward to prove. Further, if we denote shortly j_+, j_x, j_y, j_z and $j(j+1)$ for $\hat{\boldsymbol{J}}_+$, $\hat{\boldsymbol{J}}_x$, $\hat{\boldsymbol{J}}_y$, $\hat{\boldsymbol{J}}_z$ and $\hat{\boldsymbol{J}}^2$, the first six operator-equivalents $\hat{P}_{n+\tau,n}(\boldsymbol{J})$ are:

$$\begin{aligned}
\hat{P}_{n+0,n}(\boldsymbol{J}) &= j_+^n \\
\hat{P}_{n+1,n}(\boldsymbol{J}) &= \left\{j_+^n j_z\right\} \\
\hat{P}_{n+2,n}(\boldsymbol{J}) &= 2(n+1)\left\{j_+^n j_z^2\right\} - \left\{j_+^n j_x^2\right\} - \left\{j_+^n j_y^2\right\} \\
\hat{P}_{n+3,n}(\boldsymbol{J}) &= 2(n+1)\left\{j_+^n j_z^3\right\} - 3\left\{j_+^n j_z\, j_x^2\right\} - 3\left\{j_+^n j_z\, j_y^2\right\} \\
\hat{P}_{n+4,n}(\boldsymbol{J}) &= 4(n+1)(n+2)\left\{j_+^n j_z^4\right\} \\
&\quad - 12(n+2)\left\{j_+^n j_z^2 j_x^2\right\} - 12(n+2)\left\{j_+^n j_z^2\, j_y^2\right\} \\
&\quad + 3\left\{j_+^n j_x^4\right\} + 3\left\{j_+^n j_y^4\right\} + 6\left\{j_+^n j_x^2\, j_y^2\right\} \\
\hat{P}_{n+5,n}(\boldsymbol{J}) &= 4(n+1)(n+2)\left\{j_+^n j_z^5\right\} \\
&\quad - 20(n+2)\left\{j_+^n j_z^3 j_x^2\right\} - 20(n+2)\left\{j_+^n j_z^3 j_y^2\right\} \\
&\quad + 15\left\{j_+^n j_z j_x^4\right\} + 15\left\{j_+^n j_z j_y^4\right\} + 30\left\{j_+^n j_z j_x^2 j_y^2\right\}
\end{aligned} \tag{28}$$

with the convention that the symmetrization has to be symmetric concerning any permutations of j_+, j_x, j_y and j_z. Difficulties seem to arise in constructing all the permutations which the symmetrizations of (28) specify, as all of those have to be calculated independently of n. Thus, if we concentrate on constructing these permutations, it is useful to introduce curved brackets of symmetrizations which only permute the operators. They can be distinguished from the usual ones, using the number of operators they enclose as a subscript. Defining:

$$\begin{aligned}
&\left\{j_+^n j_x^a j_y^b j_z^c\right\}_{n+a+b+c} \\
&\qquad := j_+\left\{j_+^{n-1} j_x^a j_y^b j_z^c\right\}_{n+a+b+c-1} + j_x\left\{j_+^n j_x^{a-1} j_y^b j_z^c\right\}_{n+a+b+c-1} \\
&\qquad + j_y\left\{j_+^n j_x^a j_y^{b-1} j_z^c\right\}_{n+a+b+c-1} + j_z\left\{j_+^n j_x^a j_y^b j_z^{c-1}\right\}_{n+a+b+c-1}
\end{aligned} \tag{29}$$

where n, a, b and c are natural numbers greater than zero, all permutations are constructed recursively. The recursion stops if there are no more enclosed operators, i.e. the index is zero. These brackets are defined logically as one. The proof that the left-hand side of (29) is really symmetric with regard to any permutation of the operators j_+, j_x, j_y and j_z is based on the commutativity of the four terms of the sum on the right-hand side. By means of (29) we are able to justify the simplification made in (27) and to prove the, for our purpose, very useful formula:

$$\begin{aligned}
\{j_+^n j_x^a j_y^b j_z^c\}&_{n+a+b+c} \\
&= \sum_{i=0}^{n} j_+^{n-i} j_x \{j_+^i j_x^{a-1} j_y^b j_z^c\}_{i+a+b+c-1} \\
&+ \sum_{i=0}^{n} j_+^{n-i} j_y \{j_+^i j_x^a j_y^{b-1} j_z^c\}_{i+a+b+c-1} \\
&+ \sum_{i=0}^{n} j_+^{n-i} j_z \{j_+^i j_x^a j_y^b j_z^{c-1}\}_{i+a+b+c-1} .
\end{aligned} \tag{30}$$

The normal kind of symmetrizations we then find from:

$$\{j_+^n j_x^a j_y^b j_z^c\} = \frac{n!a!b!c!}{(n+a+b+c)!} \{j_+^n j_x^a j_y^b j_z^c\}_{n+a+b+c} . \tag{31}$$

A successive application of (30) reduces the calculation of symmetrizations to calculations of sums like $\sum_{i=0}^{n} i^m$, if we always commute j_+ to the left-hand side in each expression. To achieve this, we use the commutativity relations:

$$\begin{aligned}
&\forall_{n\in\mathbb{N}\setminus\{0\}} j_x j_+^n = j_+^n j_x - n j_+^{n-1}\left(\frac{n-1}{2} + j_z\right) \\
&\forall_{n\in\mathbb{N}\setminus\{0\}} j_y j_+^n = j_+^n j_y - i n j_+^{n-1}\left(\frac{n-1}{2} + j_z\right) \\
&\forall_{n\in\mathbb{N}} j_z j_+^n = j_+^n (n + j_z).
\end{aligned} \tag{32}$$

A convention has to be made with regard to the notation of the operator-equivalents $\hat{P}_{n+\tau,n}(\boldsymbol{J})$. A further application of the operator-equivalent method to (20) and (21) yields:

$$\hat{P}_{n+\tau,n}(\boldsymbol{J}) = \tfrac{1}{2}\left[\hat{H}_{n+\tau,n} j_+^n + j_+^n \hat{H}_{n+\tau,n}\right] \tag{33}$$

with

$$\hat{H}_{n+\tau,n} := H_{n+\tau,n}(j, j_z) = \sum_{\substack{v=0 \\ v \text{ even}}}^{\tau} \tilde{h}_{n\tau v}(j(j+1)) j_z^{\tau-v} \tag{34}$$

and the coefficients $\tilde{h}_{n\tau v}$ in $\hat{H}_{n+\tau,n}$ now are, compared with the coefficients $h_{n\tau v}$ in $H_{n+\tau,n}$, additionally a function of $j(j+1)$.

The recursion formalism can be easily installed on a computer: by the computer program REDUCE [12], a programmable system for formula manipulations, all symmetrizations of (28) were calculated independently of n by taking n as a variable. For the first six operators $\hat{H}_{n+\tau,n}$ we get:

$$
\begin{aligned}
\hat{H}_{n+0,n} &= 1 \\
\hat{H}_{n+1,n} &= j_z \\
\hat{H}_{n+2,n} &= (2n+3)j_z^2 - j(j+1) + \frac{n(n+1)^2}{2} - \frac{n^2(2n+3)}{2} \\
\hat{H}_{n+3,n} &= (2n+5)j_z^3 - 3j(j+1)j_z + \frac{(n+1)^2(n+2)}{2}j_z - n^2(2n+5)j_z \\
\hat{H}_{n+4,n} &= (2n+5)(2n+7)j_z^4 - 6(2n+5)j(j+1)j_z^2 \\
&\quad - (n-1)(2n+5)(3n^2+12n+5)j_z^2 \\
&\quad - 3j(j+1)(-n^3-2n^2+2n+2) + 3j^2(j+1)^2 \\
&\quad + \frac{n}{4}(5n^5+27n^4+23n^3-39n^2-10n+12) \\
\hat{H}_{n+5,n} &= (2n+7)(2n+9)j_z^5 - 10(2n+7)j(j+1)j_z^3 \\
&\quad - (2n+7)(5n^3+20n^2-15n-15)j_z^3 \\
&\quad - 5j(j+1)(-3n^3-9n^2+8n+10)j_z + 15j^2(j+1)^2j_z \\
&\quad + \tfrac{1}{4}(25n^6+185n^5+255n^4-365n^3-176n^2+172n+48)j_z.
\end{aligned}
\tag{35}
$$

If we now compare the operators $\hat{H}_{n+\tau,n}$ of (35) with the polynomial functions $H_{n+\tau,n}$ of (19), we find that the coefficient $h_{n\tau 0}$ of z^τ equals the coefficient $\tilde{h}_{n\tau 0}$ of j_z^τ. This, for the constant $\epsilon_{n+\tau,n}$, useful relation seems to hold for all τ, but is not proved explicitly.

To indicate the computer memory required for the calculations given above, the author uses a default configuration of four megabyte on an IBM 3081 computer. This was determined by the computer program REDUCE as the smallest possible configuration. By including interactively the self-written program *Qsymbol* into the program REDUCE, all six calculations were finished in six hours (nearly four hours were needed for $\hat{H}_{n+5,n}$). The author assumes that a more ingenious structure for the program *Qsymbol* should drastically decrease the required computer time.

4. Applications

4.1. Comparison with other authors

We dare say that the operator-equivalents $\hat{C}_{kq}(J)$ have their main applicability in the crystal field theory and here in particular for configurations of equivalent f electrons. As we can see by the selection rule given in (5), a set of $3+5+7=15$ operator-equivalents is in general needed to describe the crystal field splitting of an arbitrary 4f configuration. Therefore, these equivalents (and some more) have been calculated by several authors [1, 13–15], but only, and that is the difference to the operator-equivalents calculated in this paper, for fixed k *and* q. Thus, if we put special values of τ and n in the operators $\hat{H}_{n+\tau,n}$ of (35), the operator-equivalents $\hat{C}_{n+\tau,n}(J)$ should correspond to those calculated by other authors. Unfortunately, different authors use different notations and they often start their calculations using different polynomial functions or operators. To compare different operator-equivalents, we have to look carefully at their defining equations.

While by definition the so-called Stevens' operators $\hat{O}_{kq}(\boldsymbol{J})$ [1, 13], which are usually written as $\hat{O}_{kq}$, cannot be divided by any integer different from 1, the operator-equivalents $\hat{P}_{n+\tau,n}(\boldsymbol{J})$ can contain them for special values of n. If we define these integers by $\omega_{n+\tau,n}$, the following equation:

$$\hat{P}_{n+\tau,n}(\boldsymbol{J}) = \omega_{n+\tau,n}\hat{O}_{n+\tau,n}(\boldsymbol{J}) \tag{36}$$

connects both equivalents. In table 2 the $\omega_{n+\tau,n}$ are listed for $\tau = 0, 1, \ldots, 5$ and were determined by an investigation of $H_{n+\tau,n}$. A simpler relationship exists between the operator-equivalents $\hat{P}_{n+\tau,n}(\boldsymbol{J})$ and the equivalents $\hat{\hat{O}}_{n+\tau,n}(\boldsymbol{J})$, which were first introduced by Buckmaster [14] and afterwards completed by Smith and Thornley [15]. By definition we have: $\hat{\hat{O}}_{n+\tau,n}(\boldsymbol{J}) = \hat{C}_{n+\tau,n}(\boldsymbol{J})$ and therefore:

$$\hat{\hat{O}}_{n+\tau,n}(\boldsymbol{J}) = \epsilon_{n+\tau,n}\hat{P}_{n+\tau,n}(\boldsymbol{J}). \tag{37}$$

Table 2. The constants $\omega_{n+\tau,n}$ by which the operator-equivalents $\hat{P}_{n+\tau,n}(J)$ have to be divided to get the usual Stevens' operators $\hat{O}_{n+\tau,n}(J)$. If n is in the set of M, $\delta_{n,M}$ is equal to one, otherwise it is zero. The set $a\mathrm{N}+b$ is defined by $\{b, a+b, 2a+b, \ldots\}$.

$\omega_{n+0,n}$	$= 1$
$\omega_{n+1,n}$	$= 1$
$\omega_{n+2,n}$	$= 1$
$\omega_{n+3,n}$	$= 1 + 2\delta_{n,3\mathrm{N}+2}$
$\omega_{n+4,n}$	$= 1 + 2\delta_{n,3\mathrm{N}+1} + 2\delta_{n,3\mathrm{N}+2}$
$\omega_{n+5,n}$	$= \left[1 + 2\delta_{n,3\mathrm{N}+1}\right]\left[1 + 4\delta_{n,5\mathrm{N}+3} + 4\delta_{n,5\mathrm{N}+4}\right]$

4.2. Formulae for 3j-symbols as functions of their variables

The application of the Wigner–Eckart theorem to the matrix element

$$\langle jm|\hat{C}_{n+\tau,n}\ (\boldsymbol{J})|jm'\rangle$$

with $n + \tau \leq 2j$, defines a $3j$-symbol by:

$$\langle jm|\hat{C}_{n+\tau,n}(\boldsymbol{J})|jm'\rangle = (-1)^{j-m}\begin{pmatrix} j & j & n+\tau \\ m' & -m & n \end{pmatrix}\langle j\|\hat{C}_{n+\tau}(\boldsymbol{J})\|j\rangle. \tag{38}$$

The reduced matrix element is given by Smith and Thornley [15]:

$$\langle j\|\hat{C}_k(\boldsymbol{J})\|j\rangle = \frac{1}{2^k}\sqrt{\frac{(2j+k+1)!}{(2j-k)!}} \tag{39}$$

while the matrix element itself can be calculated by using equations (25), (33), (34) and the expression:

$$\langle jm|j_+^n|jm'\rangle = \delta_{m',m-n}\sqrt{\frac{(j-m+n)!}{(j+m-n)!}\frac{(j+m)!}{(j-m)!}}. \tag{40}$$

Collecting everything, we finally get:

$$\begin{aligned}\begin{pmatrix} j & j & n+\tau \\ m' & -m & n \end{pmatrix} \\ &= \delta_{m',m-n}(-1)^{j-m}2^{n+\tau}\epsilon_{n+\tau,n} \\ &\times \sqrt{\frac{(2j-n-\tau)!}{(2j+n+\tau+1)!}\frac{(j-m+n)!}{(j+m-n)!}\frac{(j+m)!}{(j-m)!}} \\ &\times \tfrac{1}{2}\left[\, H_{n+\tau,n}(j,m) + H_{n+\tau,n}(j,m-n)\right].\end{aligned} \tag{41}$$

As an example, we calculate from (35) for $\tau = 2$ and $n \leq 2j-2$:

$$\begin{aligned}\begin{pmatrix} j & j & n+2 \\ m' & -m & n \end{pmatrix} \\ &= \delta_{m',m-n}(-1)^{j-m}\frac{[2(n+2)]!}{(n+2)!}\frac{(-1)^n}{\sqrt{2!(2n+2)!}}\frac{1}{2n+3} \\ &\times \sqrt{\frac{(2j-n-2)!}{(2j+n+3)!}\frac{(j-m+n)!}{(j+m-n)!}\frac{(j+m)!}{(j-m)!}} \\ &\times \left[(2n+3)\frac{m^2+(m-n)^2}{2} - j(j+1) + \frac{n(n+1)^2}{2} - \frac{n^2(2n+3)}{2}\right].\end{aligned} \tag{42}$$

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