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The Coupling Symbols and Algebrae of Subducible, Octahedrally Projected Ligand Field Eigenvectors

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The 3Γ symbols required for the application of the Wigner-Eckart theorem to strong ligand field matrix elements are derived for complex basis functions quantized on the C_4^Z, C_3^{XYZ}, C_2^Z and C_2^{XY} axes of an octahedron. This scheme provides a standardized analysis technique for the matrix elements of subgroups in each of the four physically significant chains of the double group O_h^*. This standardization yields the minimum necessary number of ligand field parameters in any subgroup and makes possible the direct comparability of equivalent parameters in different symmetries. A unique numerical labelling for both representations and complex components on each axis provides both a simple component selection rule algebra and numerical phase factors governing permutation and conjugation of the 3Γ symbols.

Key words: Ligand field eigenvectors

1. Introduction

The formulation of quantitative series for various ligand field parameters may require comparisons of parameter values observed in complexes of different symmetries. Direct comparisons are possible when the parameters are defined using a standardized adaptation technique for each different quantization. One such standard system can be derived by projection of basis functions and operator components from the double octahedral group O_h^*. Quantization on each of the four available axes of this generative group yields orthonormal bases which are naturally subducible into most finite groups of interest [1, 2].

In this system the Hamiltonian of any subgroup of O_h^* is a sum of products of radial parameters and normalized octahedral tensor components. Each component can be realized as a normalized linear combination of spherical harmonics. These N.S.H. Hamiltonians [2] guarantee that the magnitude of any parameter remains independent of the chosen quantization G^n for any group G where n is the modulus of the quantization axis. If normalization of the operator components is neglected either the parameter changes value or the bases of the finite group must be renormalized [3].

The matrix elements of N.S.H. Hamiltonians can be factored using the Wigner-Eckart theorem [4–6]:

$$\langle\Gamma'\gamma'|\Gamma_k\gamma_k|\Gamma\gamma\rangle=(-1)^{\Gamma'-\gamma'}\begin{pmatrix}\Gamma' & \Gamma_k & \Gamma\\ \gamma' & \gamma_k & \gamma\end{pmatrix}\langle\Gamma'\|\Gamma_k\|\Gamma\rangle \quad (1)$$

By analogy with atomic vector coupling the coupling coefficients can be refactored in terms of 3Γ symbols [4]. A set of these is needed for each quantization and their properties depend on the chosen realization [4, 5]. Using a complex basis set, a numerical phase factor can be defined and the component selection rules abstracted as a finite numerical algebra [7].

2. Theory

2.1. Representation and Component Labels

For the octahedron and any of its subgroups the representation label may be uniquely assigned the lowest value of J in R_3 as $J(\Gamma_i)$, from which it is subduced. The sets of component labels can be derived from the modulus n of the chosen axis of the complex quantization. The most convenient choice of labels is centrosymmetric about $\gamma = 0$ so that

$$\gamma_{\mathrm{MAX}} = \frac{n}{2} \tag{2}$$

The value assigned to each γ_i is the minimum value of m_j appearing in the linear combination of components of R_3 up to the limit of Eq. (2). At this limit

$$-\gamma^P_{\mathrm{MAX}} \frac{2\Pi}{n} = -\frac{n}{2}\frac{2\Pi}{n} = -\Pi = \Pi = \frac{n}{2}\frac{2\Pi}{n} = \gamma^P_{\mathrm{MAX}} \frac{2\Pi}{n} \tag{3}$$

and two families of solutions $(\gamma_1^P + \gamma_2^P)$ and $(-\gamma_1^P + \gamma_2^P)$ exist. This indistinguishability is removed by recombination:

$$\begin{aligned} \gamma^{P+}_{\mathrm{MAX}} &= \frac{1}{\sqrt{2}}\left(\left|J\frac{n}{2}\right\rangle + \left|J-\frac{n}{2}\right\rangle\right) = \left(\frac{n}{2}+\right) \\ \gamma^{P-}_{\mathrm{MAX}} &= \frac{1}{\sqrt{2}}\left(\left|J\frac{n}{2}\right\rangle - \left|J-\frac{n}{2}\right\rangle\right) = \left(\frac{n}{2}-\right) \end{aligned} \tag{4}$$

when n is even, or

$$\begin{aligned} +\gamma^{P}_{\mathrm{MAX}} &= \frac{1}{\sqrt{2}}\left(\left|J\frac{n}{2}\right\rangle + i\left|J-\frac{n}{2}\right\rangle\right) = \left(\frac{n}{2}\right) \\ -\gamma^{P}_{\mathrm{MAX}} &= \frac{1}{\sqrt{2}}\left(i\left|J\frac{n}{2}\right\rangle + \left|J-\frac{n}{2}\right\rangle\right) = \left(-\frac{n}{2}\right) \end{aligned} \tag{5}$$

when n is odd.

2.2. Definition and Behaviour of 3Γ Symbols

Using these labelling conventions for both Γ_i and γ_i, the 3Γ symbols for complex bases of O_h^* can be defined;

$$\begin{pmatrix} \Gamma_1\Gamma_2\Gamma_3 \\ \gamma_1\gamma_2\gamma_3^* \end{pmatrix} = (-1)^{(J(\Gamma_1)-J(\Gamma_2)+\gamma_3^*)}\,\lambda[\Gamma]^{-1/2}\langle\Gamma \quad \Gamma_2\gamma_2|\Gamma_3\gamma_3\rangle \tag{6}$$

in which $\lambda[\Gamma]$ is the degeneracy of Γ. For odd order quantization axes;

$$(\gamma)^* = -\gamma . (-1)^{\gamma} \tag{7}$$

and for even order axes;

$$(\gamma +)^* = \gamma^+ . (-1)^{\gamma} \tag{8}$$

but

$$(\gamma -)^* = \gamma^- . (-1)^{\gamma+1}$$

To minimize the size of the tables of 3Γ symbols, the conjugation and permutation properties are defined using these phase conventions. From the general form of conjugation behaviour [8].

$$\begin{pmatrix} \Gamma_1 \Gamma_2 \Gamma_3 \\ \gamma_1^* \gamma_2^* \gamma_3^* \end{pmatrix} = (-1)^{J(\Gamma_1)+J(\Gamma_2)+J(\Gamma_3)+\gamma_1^*+\gamma_2^*+\gamma_3^*} \begin{pmatrix} \Gamma_1 \Gamma_2 \Gamma_3 \\ \gamma_1 \gamma_2 \gamma_3 \end{pmatrix} \tag{9}$$

this is identical to negation except for components labelled $(\gamma-)$ which do not change sign. The general form for permutation of columns is

$$\begin{pmatrix} \Gamma_1 \Gamma_2 \Gamma_3 \\ \gamma_1 \gamma_2 \gamma_3 \end{pmatrix} = (-1)^{[J(\Gamma_1)+J(\Gamma_2)+J(\Gamma_3)]} \begin{pmatrix} \Gamma_1 \Gamma_2 \Gamma_3 \\ \gamma_1 \gamma_3 \gamma_2 \end{pmatrix} \tag{10}$$

which is equivalent to that of V coefficients [5] when the symmetric or antisymmetric squares of representations are defined.

2.3. Algebra of 3Γ Symbols

a) The representations are combined using the conventional Kronecker triple product rules [5].
b) The component algebra is identical to that of 3-*j* symbols [8] except when $\gamma_i = \pm n/2$. A more complete statement of the component algebra is:

$$\mathrm{mod}_n(\gamma_1 + \gamma_2) = -\mathrm{mod}_n(\gamma_3^*) \tag{11}$$

This rule permits 3Γ symbols with two identical columns and an odd representation sum, $\Sigma_i J(\Gamma_i)$, to exist, unlike such analogous 3-*j* symbols [8], if

$$(-1)[\gamma_1^* + \gamma_2^* + (\gamma_3^*)^*] = (-1) \tag{12}$$

This condition occurs in 3Γ symbols with two $|\gamma-\rangle$ components and was seen in previous selection rule schemes involving components labelled $|0-\rangle$ [5].

2.4. Selection Rules under Specific Quantizing Axes of O_h^*

The selection, permutation and negation rules of 3Γ symbols for basis functions on each quantizing axis are changed from the 3-*j* behaviour [8] according to the value of γ_{MAX}.

Table 1. C_4^z 3Γ Symbols

Γ_1	Γ_2	Γ_3	γ_1	γ_2	γ_3^*	$(\text{Val})^2$	Perm.[b]	Conj.[c]
E'	E'	T_1	1/2	1/2	−1	* 1/3[d]	0	0
E'	E'	A_1	1/2	−1/2	0	1/2	1	1
E'	E'	T_1	1/2	−1/2	0	1/6	0	0
E'	G	E	1/2	3/2	2+	* 1/4	0	0
E'	G	T_2	1/2	3/2	2−	1/6	0	1
E'	G	T_1	1/2	1/2	−1	1/12	1	1
E'	G	T_2	1/2	1/2	−1	1/4	0	0
E'	G	T_1	1/2	−1/2	0	* 1/6	1	1
E'	G	E	1/2	−1/2	0	* 1/4	0	0
E	G	T_1	1/2	−3/2	1	1/4	1	1
E	G	T_2	1/2	−3/2	1	1/12	0	0
E'	E''	A_2	1/2	3/2	2−	* 1/2	0	1
E'	E''	T_2	1/2	3/2	2−	* 1/6	1	0
E'	E''	T_2	1/2	−3/2	−1	* 1/3	1	1
G	G	T_1	3/2	3/2	1	* 5/48	n[a]	n[a]
G	G	T_2	3/2	3/2	1	3/48	n	n
G	G	E	3/2	1/2	2+	1/8	1	1
G	G	T_2	3/2	1/2	2−	* 1/12	n	$n+1$
G	G	A_2	3/2	1/2	2−	* 1/4	0	1
G	G	T_1	3/2	−1/2	−1	* 1/16	n	n
G	G	T_2	3/2	−1/2	−1	* 5/48	n	n
G	G	A_1	3/2	−3/2	0	1/4	1	1
G	G	E	3/2	−3/2	0	1/8	1	1
G	G	T_1	3/2	−3/2	0	1/12	n	n
G	G	T_1	1/2	1/2	−1	5/48	n	n
G	G	T_2	1/2	1/2	−1	3/48	n	n
G	G	A_1	1/2	−1/2	0	1/4	1	1
G	G	T_1	1/2	−1/2	0	1/12	n	n
G	G	E	1/2	−1/2	0	1/8	1	1
G	E''	T_1	3/2	3/2	1	* 1/12	1	1
G	E''	T_2	3/2	3/2	1	* 1/4	0	0
G	E''	T_1	3/2	−3/2	0	* 1/6	1	1
G	E''	E	3/2	−3/2	0	* 1/4	0	0
G	E''	E	1/2	3/2	2+	1/4	0	0
G	E''	T_2	1/2	3/2	2−	1/6	0	1
G	E''	T_1	1/2	−3/2	1	* 1/6	1	1
G	E''	T_2	1/2	−3/2	1	1/6	0	0
E''	E''	T_1	3/2	3/2	1	* 1/3	0	0
E''	E''	A_1	3/2	−3/2	0	1/2	1	1
E''	E''	T_1	3/2	−3/2	0	* 1/6	0	0
T_1	T_1	E	1	1	2+	1/4	0	0
T_1	T_1	T_2	1	1	2−	* 1/6	0	1
T_1	T_1	T_1	1	0	−1	* 1/6	1	1
T_1	T_1	T_2	1	0	−1	* 1/6	0	1
T_1	T_1	A_1	1	−1	0	1/3	0	0
T_1	T_1	E	1	−1	0	1/12	0	0
T_1	E	T_2	1	0	−1	1/4	1	1
T_1	E	T_2	1	2+	1	1/12	1	1
T_1	T_2	A_2	1	1	2−	1/3	0	1
T_1	T_2	T_2	1	1	2−	1/6	1	0
T_1	T_1	A_1	0	0	0	1/3	0	0
T_1	T_1	E	0	0	0	1/3	0	0
T_1	E	T_2	0	2+	2−	* 1/3	1	0
T_1	T_2	A_2	0	2−	2−	1/3	0	0
E	E	A_1	0	0	0	1/2	0	0

Table 1.—*continued*

Γ_1	Γ_2	Γ_3	γ_1	γ_2	γ_3^*	$(\text{Val})^2$	Perm.[b]	Conj.[c]
E	E	E	0	0	0	1/4	0	0
E	E	E	0	2+	2+	1/4	0	0
E	E	A_2	0	2+	2−	1/2	1	0
E	T_2	T_2	0	1	−1	1/2	0	0
E	T_2	T_2	0	2−	2−	* 1/3	0	0
E	E	A_1	2+	2+	0	1/2	0	0
E	T_2	T_2	2+	1−	1	1/6	0	0
T_2	T_2	T_2	1	2−	1	1/6	0	1
A_2	A_2	A_1	2−	2−	0	1	0	0
A_1	A_1	A_1	0	0	0	1	0	0

[a] $n = \Sigma_i J_i$ where J_i are the actual J not the $J(\Gamma_i)$ since $G \times G$ is not simply reducible.
[b] perm. = behaviour under interchange of adjacent columns.
[c] conj. = behaviour under "negation" of all components (see text).
[d] * = square root is negative.

C_4^Z - Selection and permutation rules follow 3-j behaviour. Conjugation behaviour for 3Γ symbols with one or three $|2-\rangle$ components is opposite to permutation. These properties are noted in the tables as 0 or 1 for even or odd behaviour under either operation.

C_3^{XYZ} - The behaviour of 3Γ symbols for components of weakly adapted bases is identical to that of 3-j symbols. Strongly adapted bases involve special definition problems not considered here.

C_2 - Under any C_2 quantization only three component labels 1 −, 0, 1 + should be allowed. Since the system is also adapted to O_h^* two C_2 axes can be distinguished and further component labels introduced.

C_2^Z - The coincident C_4^Z divides the self conjugate components into three subclasses;

odd special components $1 \pm (= n/2)$
even special components 0
even special components $2\pm$

No integer components with natural signs exist and the natural sign of special components is always taken positive in (11).
The special rules permit the four symbols

$$\begin{pmatrix} T_1 T_2 T_2 \\ 1\pm 1\pm 2- \end{pmatrix} \text{ and } \begin{pmatrix} T_1 T_2 A_2 \\ 1\pm 1\pm 2- \end{pmatrix}$$

to exist

C_2^{XY} - The absence of a C_4 axis permits a redistribution of component labels. These are $0\pm$ and $1\pm$, the $0-$ being identified with $2-$ in the tables. The selection rules are the same as for C_2^Z quantization.

2.5. Evaluation of Existing 3Γ Symbols

The sign and magnitude of 3Γ symbols were defined [1] in a previous paper in terms of a product of Subduction Coefficients, a normalization constant and the appropriate

Table 2. C_3^{xyz} 3Γ coefficients (weakly adapted)

Γ_1	Γ_2	Γ_3	γ_1	γ_2	γ_3^*		(Val)^2	Perm.	Conj.
E'	E'	T_1	1/2	1/2	−1	*	1/3	0	0
E'	E'	A_1	1/2	−1/2	0		1/2	1	1
E'	E'	T_1	1/2	−1/2	0		1/6	0	0
E'	G	E	1/2	3/2	1		1/6	0	1[a]
E'	G	T_2	1/2	3/2	1	*	1/3	0	1
E'	G	T_1	1/2	1/2	−1		1/12	1	1
E'	G	E	1/2	1/2	−1		1/2	0	0
E'	G	T_2	1/2	1/2	−1		1/12	0	0
E'	G	T_1	1/2	−1/2	0	*	1/6	1	1
E'	G	T_2	1/2	−1/2	0	*	1/6	0	0
E'	G	T_1	1/2	−3/2	1		1/2	1	1
E'	G	E	1/2	−3/2	1		1/12	0	0
E'	G	T_2	1/2	−3/2	1		1/36	0	0
E'	E''	T_2	1/2	1/2	−1	*	1/3	1	1
E'	E''	A_2	1/2	−1/2	0		1/2	0	0
E'	E''	T_2	1/2	−1/2	0		1/6	1	1
G	G	A_1	3/2	3/2	0	*	2/3	n[b]	$n+1$
G	G	T_1	3/2	3/2	0		5/54	n	$n+1$
G	G	T_2	3/2	3/2	0		1/6	n	$n+1$
G	G	T_1	3/2	1/2	+1	*	5/36	n	$n+1$
G	G	T_2	3/2	1/2	+1		5/36	n	$n+1$
G	G	E	3/2	1/2	+1		1/12	n	$n+1$
G	G	T_1	3/2	−1/2	−1	*	1/3	n	n
G	G	T_2	3/2	−1/2	−1	*	1/3	n	n
G	G	E	3/2	−1/2	−1	*	1/6	n	n
G	G	T_1	3/2	−3/2	0		17/72	n	n
G	G	T_2	3/2	−3/2	0		1/12	n	n
G	G	A_2	3/2	−3/2	0		1/36	n	n
G	G	A_1	3/2	−3/2	0		1/4	n	n
G	G	T_1	1/2	1/2	−1		1/6	n	n
G	G	T_2	1/2	1/2	−1	*	1/6	n	n
G	G	T_1	1/2	−1/2	0	*	1/12	n	n
G	G	T_2	1/2	−1/2	0		1/12	n	n
G	G	A_2	1/2	−1/2	0		1/4	n	n
G	G	A_1	1/2	−1/2	0	*	1/4	n	n
G	E''	T_1	3/2	1/2	1		2/9	1	0
G	E''	E	3/2	1/2	1		1/6	0	1
G	E''	T_1	3/2	−1/2	−1		1/36	1	1
G	E''	T_2	3/2	−1/2	−1		1/2	0	0
G	E''	E	3/2	−1/2	−1		1/12	0	0
G	E''	T_1	1/2	1/2	−1	*	1/12	1	1
G	E''	T_2	1/2	1/2	−1		1/12	0	0
G	E''	E	1/2	1/2	−1	*	1/2	0	0
G	E''	T_1	1/2	−1/2	0		1/6	1	1
G	E''	T_2	1/2	−1/2	0		1/6	0	0
E''	E''	T_1	1/2	1/2	−1		1/3	0	0
E''	E''	T_1	1/2	−1/2	0	*	1/6	0	0
E''	E''	A_1	1/2	−1/2	0		1/2	1	1
T_1	T_1	E	1	1	1	*	1/6	0	1
T_1	T_1	T_2	1	1	1		2/9	0	1
T_1	T_1	T_1	1	0	−1	*	1/6	1	1

Table 2.—*continued*

Γ_1	Γ_2	Γ_3	γ_1	γ_2	γ_3^*	$(\text{Val})^2$	Perm.	Conj.
T_1	T_1	T_2	1	0	–1	* 1/18	0	0
T_1	T_1	E	1	0	–1	* 1/6	0	0
T_1	T_1	A_1	1	–1	0	1/3	0	0
T_1	T_1	T_1	1	–1	0	1/6	1	1
T_1	T_1	T_2	1	–1	0	1/18	0	0
T_1	T_1	A_1	0	0	0	* 1/3	0	0
T_1	T_1	T_2	0	0	0	2/9	0	0
T_1	T_2	T_1	1	1	1	2/9	0	1
T_1	T_2	E	1	1	1	1/6	1	0
T_1	T_2	T_1	1	0	–1	1/18	0	0
T_1	T_2	T_2	1	0	–1	1/6	1	1
T_1	T_2	E	1	0	–1	1/6	1	1
T_1	T_2	T_1	1	–1	0	* 1/18	0	0
T_1	T_2	T_2	1	–1	0	* 1/6	1	1
T_1	T_2	A_2	1	–1	0	* 1/3	0	0
T_1	T_2	T_1	0	0	0	2/9	0	0
T_1	T_2	A_2	0	0	0	* 1/3	0	0
T_1	E	T_1	1	1	1	* 1/6	0	1
T_1	E	T_2	1	1	1	* 1/6	1	0
T_1	E	T_1	1	–1	0	* 1/6	0	0
T_1	E	T_2	1	–1	0	* 1/6	1	1
T_1	E	T_1	0	1	–1	* 1/6	0	0
T_1	E	T_2	0	1	–1	* 1/6	1	1
T_1	E	T_1	0	–1	1	* 1/6	0	0
T_1	E	T_2	0	–1	1	1/6	1	1
E	E	E	1	1	1	1/2	0	1
E	E	A_1	1	–1	0	1/2	0	0
E	E	A_2	1	–1	0	1/2	1	1
E	T_2	T_1	1	1	1	* 1/6	1	0
E	T_2	T_2	1	1	1	* 1/6	0	1
E	T_2	T_1	1	0	–1	1/6	1	1
E	T_2	T_2	1	0	–1	1/6	0	0
E	T_2	T_1	1	–1	0	* 1/6	1	1
E	T_2	T_2	1	–1	0	1/6	0	0
T_2	T_2	T_2	1	1	1	* 2/9	0	1
T_2	T_2	E	1	1	1	* 1/6	0	1
T_2	T_2	T_1	1	0	–1	1/6	1	1
T_2	T_2	T_2	1	0	–1	* 1/18	0	0
T_2	T_2	E	1	0	–1	1/6	0	0
T_2	T_2	T_1	1	–1	0	1/6	1	1
T_2	T_2	T_2	1	–1	0	* 1/18	0	0
T_2	T_2	A_1	1	–1	0	* 1/3	0	0
T_2	T_2	A_1	0	0	0	1/3	0	0
T_2	T_2	T_2	0	0	0	* 2/9	0	0
A_2	A_2	A_1	0	0	0	1	0	0
A_1	A_1	A_1	0	0	0	1	0	0

[a] Because of Eq. (11), whenever $\gamma_1 + \gamma_2 + \gamma_3 = 3$ the 3Γ coefficient exists but its conjugation behaviour is the reverse of its permutation behaviour.

[b] $n = \Sigma_i J_i$ where J_i are the actual J not the $J(\Gamma_i)$.

Table 3. C_2^z 3Γ coefficients

Γ_1	Γ_2	Γ_3	γ_1	γ_2	γ_3^*	$(\mathrm{Val})^2$	Perm.	Conj.
E'	E'	T_1	1/2	1/2	1+	* 1/6	0	0
E'	E'	T_1	1/2	1/2	1−	* 1/6	0	1
E'	E'	A_1	1/2	−1/2	0	* 1/2	1	1
E'	E'	T_1	1/2	−1/2	0	1/6	0	0
E'	G	E	1/2	3/2	2+	* 1/4	0	0
E'	G	T_2	1/2	3/2	2−	1/6	0	1
E'	G	T_1	1/2	1/2	1+	1/24	1	1
E'	G	T_1	1/2	1/2	1−	1/24	1	0
E'	G	T_2	1/2	1/2	1+	3/24	0	0
E'	G	T_2	1/2	1/2	1−	3/24	0	1
E'	G	T_1	1/2	−1/2	0	* 1/6	1	1
E'	G	E	1/2	−1/2	0	* 1/4	0	0
E'	G	T_1	1/2	−3/2	1+	3/24	1	1
E'	G	T_1	1/2	−3/2	1−	* 3/24	1	0
E'	G	T_2	1/2	−3/2	1+	1/24	0	0
E'	G	T_2	1/2	−3/2	1−	* 1/24	0	1
E'	E''	T_2	1/2	3/2	2−	* 1/6	1	0
E'	E''	A_2	1/2	3/2	2−	* 1/2	0	1
E'	E''	T_2	1/2	−3/2	1+	* 1/6	0	0
E'	E''	T_2	1/2	−3/2	1−	1/6	0	1
G	G	T_1	3/2	3/2	1+	* 5/96	n	n
G	G	T_1	3/2	3/2	1−	5/96	n	$n+1$
G	G	T_2	3/2	3/2	1+	* 3/96	n	n
G	G	T_2	3/2	3/2	1−	* 3/96	n	$n+1$
G	G	E	3/2	1/2	2+	1/8	0	0
G	G	T_2	3/2	1/2	2−	−1/12	n	$n+1$
G	G	A_2	3/2	1/2	2−	1/4	n	$n+1$
G	G	T_1	3/2	−1/2	1+	* 3/96	n	n
G	G	T_1	3/2	−1/2	1−	* 3/96	n	$n+1$
G	G	T_2	3/2	−1/2	1+	* 5/96	n	n
G	G	T_2	3/2	−1/2	1−	* 5/96	n	$n+1$
G	G	A_1	3/2	−3/2	0	−1/4	1	1
G	G	T_1	3/2	−3/2	0	1/12	n	n
G	G	E	3/2	−3/2	0	1/8	1	1
G	G	T_1	1/2	1/2	1+	5/96	n	n
G	G	T_1	1/2	1/2	1−	5/96	n	$n+1$
G	G	T_2	1/2	1/2	1+	* 3/96	n	n
G	G	T_2	1/2	1/2	1−	3/96	n	$n+1$
G	G	A_1	1/2	−1/2	0	* 1/4	1	1
G	G	T_1	1/2	−1/2	0	* 1/12	n	n
G	G	E	1/2	−1/2	0	1/8	1	1
G	E''	T_1	3/2	3/2	1+	* 1/24	1	1
G	E''	T_1	3/2	3/2	1−	1/24	1	0
G	E''	T_2	3/2	3/2	1+	* 3/24	0	0
G	E''	T_2	3/2	3/2	1−	3/24	0	1
G	E''	T_1	3/2	−3/2	0	* 1/6	1	1
G	E''	E	3/2	−3/2	0	* 1/4	0	0
G	E''	E	1/2	3/2	2+	1/4	0	0
G	E''	T_2	1/2	3/2	2−	* 1/6	0	1
G	E''	T_1	1/2	−3/2	1+	* 3/24	1	1
G	E''	T_1	1/2	−3/2	1−	* 3/24	1	0
G	E''	T_2	1/2	−3/2	1−	1/24	0	0
G	E''	T_2	1/2	−3/2	1−	* 1/24	0	1
E''	E''	T_1	3/2	3/2	1+	1/6	0	0
E''	E''	T_1	3/2	3/2	1−	* 1/6	0	1

Table 3.–*continued*

Γ_1	Γ_2	Γ_3	γ_1	γ_2	γ_3	$(\text{Val})^2$	Perm.	Conj.
E''	E''	A_1	3/2	−3/2	0	* 1/2	1	1
E''	E''	T_1	3/2	−3/2	0	* 1/6	0	0
T_1	T_1	A_1	1+	1+	0	1/3	0	0[a]
T_1	T_1	E	1+	1+	0	1/3	0	
T_1	T_1	T_1	1+	0	1−	* 1/6	1	
T_1	T_1	T_2	1+	0	1+	* 1/6	0	
T_1	T_1	T_1	1+	1−	0	1/6	1	
T_1	T_1	T_2	1+	1−	2−	* 1/6	0	
T_1	T_1	A_1	0	0	0	* 1/3	0	
T_1	T_1	E	0	0	0	1/3	0	
T_1	T_1	T_1	0	1−	1+	* 1/6	1	
T_1	T_1	T_2	0	1−	1−	1/6	0	
T_1	T_1	A_1	1−	1−	0	* 1/3	0	
T_1	T_1	E	1−	1−	0	* 1/12	0	
T_1	T_1	E	1−	1−	2+	1/4	0	
T_1	E	T_1	1+	0	1+	1/12	0	
T_1	E	T_2	1+	0	1−	1/4	1	
T_1	E	T_1	1+	2+	1+	1/4	0	
T_1	E	T_2	1+	2+	1−	* 1/12	1	
T_1	E	T_1	0	0	0	1/3	0	
T_1	E	T_2	0	2+	2−	* 1/3	1	
T_1	E	T_1	1−	0	1−	* 1/12	0	
T_1	E	T_2	1−	0	1+	* 1/4	1	
T_1	E	T_1	1−	2+	1−	1/4	0	
T_1	E	T_2	1−	2+	1+	* 1/12	1	
T_1	T_2	T_1	1+	1+	0	* 1/6	0	
T_1	T_2	T_2	1+	1+	2−	1/6	1	
T_1	T_2	T_1	1+	2−	1−	1/6	0	
T_1	T_2	T_2	1+	2−	1+	1/6	1	
T_1	T_2	E	1+	1−	0	* 1/4	1	
T_1	T_2	E	1+	1−	2+	1/12	1	
T_1	T_2	T_1	0	1+	1+	* 1/6	0	
T_1	T_2	T_2	0	1+	1−	* 1/6	1	
T_1	T_2	E	0	2−	2+	1/3	1	
T_1	T_2	A_2	0	2−	2−	1/3	0	
T_1	T_2	T_1	0	1−	1−	1/6	0	
T_1	T_2	T_2	0	1−	1+	1/6	1	
T_1	T_2	E	1−	1+	0	1/4	1	
T_1	T_2	E	1−	1+	2+	1/12	1	
T_1	T_2	A_2	1−	1+	2−	* 1/3	0	
T_1	T_2	T_1	1−	2−	1+	1/6	0	
T_1	T_2	T_2	1−	2−	1−	* 1/6	1	
T_1	T_2	T_1	1−	1−	0	1/6	0	
T_1	T_2	T_2	1−	1−	2−	1/6	1	
E	E	A_1	0	0	0	1/2	0	
E	E	E	0	0	0	* 1/4	0	
E	E	E	0	2+	2+	1/4	0	
E	E	A_2	0	2+	2−	1/2	1	
E	T_2	T_1	0	1+	1−	* 1/4	1	
E	T_2	T_2	0	1+	1+	1/12	0	
E	T_2	T_2	0	2−	2−	* 1/3	0	
E	T_2	T_1	0	1−	1+	1/4	0	
E	T_2	T_2	0	1−	1−	* 1/12	0	
E	E	A_1	2+	2+	0	1/2	0	
E	E	E	2+	2+	0	1/2	0	

Table 3.—*continued*

Γ_1	Γ_2	Γ_3	γ_1	γ_2	γ_3	$(\mathrm{Val})^2$	Perm.	Conj.
E	T_2	T_1	2+	1+	1−	* 1/12	1	
E	T_2	T_2	2+	1+	1+	* 3/4	0	
E	T_2	T_1	2+	2−	0	* 1/3	0	
E	T_2	T_1	2+	2−	0	* 1/3	1	
E	T_2	T_2	2+	1−	1−	* 1/4	0	
E	T_2	T_2	2+	1−	1−	* 3/4	0	
T_2	T_2	A_1	1+	1+	A_1	* 1/3	0	
T_2	T_2	E	1+	1+	0	1/12	0	
T_2	T_2	E	1+	1+	2+	* 1/4	0	
T_2	T_2	T_1	1+	2−	1+	1/6	1	
T_2	T_2	T_2	1+	2−	1−	* 1/6	0	
T_2	T_2	T_1	1+	1−	0	* 1/6	1	
T_2	T_2	T_2	1+	1−	2−	* 1/6	0	
T_2	T_2	A_1	2−	2−	0	* 1/3	0	
T_2	T_2	E	2−	2−	0	* 1/3	0	
T_2	T_2	T_1	2−	1−	1−	* 1/6	1	
T_2	T_2	T_2	2−	1−	1+	* 1/6	0	
T_2	T_2	A_1	1−	1−	0	1/3	0	
T_2	T_2	E	1−	1−	0	* 1/12	0	
T_2	T_2	E	1−	1−	2+	1/4	0	
A_2	A_2	A_1	2−	2−	0	1	0	
A_1	A_1	A_1	0	0	0	1	0	

[a] For all two-fold components, behaviour under conjugation must be even for a 3Γ composed of 3 integer reps to exist.

3-*j* symbol. This procedure is possible if the ratio of the intermediate coupling coefficients is a constant, independent of all J_i:

$$\frac{\langle J_1\Gamma_1\gamma_1, J_2\Gamma_2\gamma_2 | J_3\Gamma_3\gamma_3\rangle}{\langle J_1\Gamma_1\gamma_1', J_2\Gamma_2\gamma_2' | J_3\Gamma_3\gamma_3'\rangle} = \frac{\sum_{M_i} S(M_1)^* SM_2 SM_3 \begin{pmatrix} J_1 & J_2 & J_3 \\ -M_1 & M_2 & M_3 \end{pmatrix} (-1)^{M-M_1'}}{\sum_{M_i'} S(M_1')^* SM_2' SM_3' \begin{pmatrix} J_1 & J_2 & J_3 \\ -M_1' & M_2' & M_3' \end{pmatrix}} = \frac{\begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix}}{\begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma_3 \\ \gamma_1' & \gamma_2' & \gamma_3' \end{pmatrix}} \tag{13}$$

This ratio is constant when the basis set is quantized to a simply reducible tail group of a physically significant [9] chain. This is the case for an O_h^{*4} or O_h^{*2} quantization since C_{4v}^* and C_{2v}^* are both simply reducible. However, C_{3v}^* is not simply reducible and it is not possible to define invariant [10] 3Γ symbols in a strong adaptation to the C_3^{XYZ} axis. Weak adaptation, truncating the chain at D_{3d}^* does yield 3Γ symbols since D_{3d}^* is isomorphous with the simply reducible group D_{3h}^*. This appeal to D_{3h}^* is formalization of the process of transduction defined earlier [1]. It is these 3Γ symbols defined in the weakly adapted trigonal bases that are given in Table 2.

Table 4. C_2^{xy} 3Γ symbols

Γ_1	Γ_2	Γ_3	γ_1	γ_2	γ_3	(Value)^2	Perm.	Conj.
E'	E'	T_1	1/2	1/2	1+	* 1/6	0	0
E'	E'	T_1	1/2	1/2	1−	* 1/6	0	1
E'	E'	A_1	1/2	−1/2	0	1/2	1	1
E'	E'	T_1	1/2	−1/2	0	1/6	0	0
E'	G	E	1/2	3/2	0	* 3/16	0	0
E'	G	T_2	1/2	3/2	0	* 1/6	0	0
E'	G	T_2	1/2	3/2	0−	* 1/24	0	1
E'	G	T_1	1/2	1/2	1+	1/24	1	1
E'	G	T_1	1/2	1/2	1−	1/24	1	0
E'	G	E	1/2	1/2	1−	* 3/16	0	1
E'	G	T_2	1/2	1/2	1+	1/8	0	0
E'	G	T_1	1/2	−1/2	0	* 1/6	1	1
E'	G	E	1/2	−1/2	0	* 1/16	0	0
E'	G	T_2	1/2	−1/2	0	* 1/8	0	0
E'	G	T_1	1/2	−3/2	1+	1/8	1	1
E'	G	T_1	1/2	−3/2	1−	* 1/8	1	0
E'	G	E	1/2	−3/2	1−	1/16	0	1
E'	G	T_2	1/2	−3/2	1+	1/24	0	0
E'	E''	A_2	1/2	1/2	1+	* 1/2	0	0
E'	E''	T_2	1/2	1/2	1+	* 1/6	1	1
E'	E''	T_2	1/2	−1/2	0−	* 1/6	1	0
E'	E''	T_2	1/2	−1/2	0	* 1/6	1	1
G	G	A_2	3/2	3/2	1+	3/16	n	n
G	G	T_1	3/2	3/2	1+	* 5/96	n	n
G	G	T_1	3/2	3/2	1−	* 5/384	n	$n+1$
G	G	T_2	3/2	3/2	1+	9/128	n	n
G	G	E	3/2	1/2	0	3/32	1	1
G	G	T_2	3/2	1/2	0	*29/384	n	n
G	G	T_2	3/2	1/2	0−	*17/384	n	$n+1$
G	G	T_1	3/2	1/2	0	5/128	n	n
G	G	T_1	3/2	−1/2	1+	* 1/32	n	n
G	G	T_1	3/2	−1/2	1−	* 5/128	n	$n+1$
G	G	E	3/2	−1/2	1−	1/8	1	0
G	G	A_2	3/2	−1/2	1+	* 1/16	0	0
G	G	T_2	3/2	−1/2	1+	*17/384	n	n
G	G	A_1	3/2	−3/2	0	1/4	1	1
G	G	T_1	3/2	−3/2	0	29/384	n	n
G	G	E	3/2	−3/2	0	1/32	1	1
G	G	T_2	3/2	−3/2	0	1/32	n	n
G	G	T_2	3/2	−3/2	0−	1/128	n	$n+1$
G	E''	T_1	3/2	1/2	0	* 1/24	1	1
G	E''	E	3/2	1/2	0	* 1/16	0	0
G	E''	T_2	3/2	1/2	0	* 1/8	0	0
G	E''	T_2	3/2	1/2	2−	1/8	0	1
G	E''	T_1	3/2	−1/2	1+	* 1/24	1	1
G	E''	T_1	3/2	−1/2	1−	* 1/6	1	0
G	E''	E	3/2	−1/2	1−	* 3/16	0	1
G	G	T_1	1/2	1/2	1+	5/96	n	n
G	G	T_1	1/2	1/2	1−	29/384	n	$n+1$
G	G	A_2	1/2	1/2	1+	* 3/16	0	0
G	G	T_2	1/2	1/2	1+	* 1/128	n	n
G	G	A_1	1/2	−1/2	0	* 1/4	1	1
G	G	T_1	1/2	−1/2	0	* 5/384	n	n
G	G	E	1/2	−1/2	0	1/32	1	1
G	G	T_2	1/2	−1/2	0	1/32	n	n

Table 4.—*continued*

Γ_1	Γ_2	Γ_3	γ_1	γ_2	γ_3	(Value)^2	Perm.	Conj.
G	G	T_2	1/2	−1/2	0−	* 3/128	n	$n+1$
G	E''	T_1	1/2	−1/2	0	1/8	1	1
G	E''	E	1/2	−1/2	0	3/16	0	0
G	E''	T_2	1/2	−1/2	0	* 1/24	0	0
G	E''	T_2	1/2	−1/2	0−	1/24	0	1
G	E''	T_1	1/2	1/2	1+	* 1/8	1	1
G	E''	E	1/2	1/2	1−	1/16	0	1
G	E''	T_2	1/2	1/2	1+	* 1/6	0	0
E''	E''	T_1	1/2	1/2	1+	1/6	0	0
E''	E''	T_1	1/2	1/2	1−	* 1/6	0	1
E''	E''	T_1	1/2	−1/2	0	1/6	0	0
E''	E''	A_1	1/2	−1/2	0	1/2	1	1
T_1	T_1	A_1	1+	1+	0	1/3	0	0[a]
T_1	T_1	E	1+	1+	0	1/3	0	0
T_1	T_1	T_1	1+	0	1−	* 1/6	1	
T_1	T_1	T_2	1+	0	1+	1/6	0	
T_1	T_1	T_1	1+	1−	0	1/6	1	
T_1	T_1	T_2	1+	1−	0−	1/6	0	
T_1	E	T_1	1+	0	1+	1/3	0	
T_1	E	T_2	1+	1−	0	1/3	1	
T_1	T_2	T_1	1+	0−	1−	1/6	0	
T_1	T_2	T_2	1+	0−	1+	1/6	1	
T_1	A_2	T_2	1+	1+	0	1/3	0	
T_1	T_1	A_1	0	0	0	1/3	0	
T_1	T_1	E	0	0	0	1/12	0	
T_1	T_1	T_2	0	0	0	1/6	0	
T_1	T_1	T_1	0	1−	1+	* 1/6	1	
T_1	T_1	E	0	1−	1+	* 1/4	0	
T_1	E	T_1	0	0	0	1/12	0	
T_1	E	T_2	0	0	0−	* 1/4	1	
T_1	E	T_1	0	1−	1−	1/4	0	
T_1	E	T_2	0	1−	1+	* 1/12	1	
T_1	T_2	E	0	0−	0	1/4	1	
T_1	T_2	T_2	0	0−	0	* 1/6	1	
T_1	T_2	T_1	0	1+	1+	* 1/6	0	
T_1	T_2	E	0	1+	1−	1/12	1	
T_1	T_2	A_2	0	1+	1+	1/3	0	
T_1	T_2	T_1	0	0	0	1/6	0	
T_1	T_2	T_2	0	0	0−	1/6	1	
T_1	T_1	T_2	1−	1−	0	* 1/6	0	
T_1	T_2	T_2	1−	1+	0	1/6	1	
E	E	A_1	0	0	0	1/2	0	
E	E	E	0	0	0	1/4	0	
E	E	E	0	1−	1−	* 1/2	0	
E	E	A_2	0	1−	1+	1/3	1	
E	T_2	T_1	0	0−	0	* 1/4	1	
E	T_2	T_2	0	0−	0−	* 1/12	0	
E	T_2	T_1	0	1+	1−	* 1/4	1	
E	T_2	T_2	0	1+	1+	* 1/12	0	
E	T_2	T_2	0	0	0	* 1/3	0	
E	A_2	E	0	1+	1−	* 1/2	1	
E	E	A_1	1−	1−	0	* 1/2	0	
E	E	E	1−	1−	0	* 1/4	0	
E	T_2	T_1	1−	0−	1−	* 1/12	1	
E	T_2	T_2	1−	0−	1+	1/4	0	

Table 4.—*continued*

Γ_1	Γ_2	Γ_3	γ_1	γ_2	γ_3	(Value)^2	Perm.	Conj.
E	T_2	T_1	1−	1+	0	* 1/12	1	
E	T_2	T_2	1−	1+	0−	1/4	0	
E	T_2	T_1	1−	0	1+	1/3	1	
E	A_2	E	1−	1+	0	1/2	1	
T_2	T_2	A_1	0−	0−	0	* 1/3	0	
T_2	T_2	E	0−	0−	0	* 1/12	0	
T_2	T_2	T_2	0−	0−	0	* 1/6	0	
T_2	T_2	E	0−	1+	1−	1/4	0	
T_2	T_2	T_1	0−	1+	1+	* 1/6	1	
T_2	T_2	T_1	0−	0	0	* 1/6	1	
T_2	T_2	T_2	0−	0	0−	* 1/6	0	
T_2	T_2	A_1	1+	1+	0	* 1/3	0	
T_2	T_2	E	1+	1+	0	* 1/12	0	
T_2	T_2	T_2	1+	1+	0	* 1/6	0	
T_2	T_2	T_1	1+	0	1−	1/6	1	
T_2	T_2	T_2	1+	0	1+	1/6	0	
T_2	A_2	T_1	1+	1+	0	1/3	0	
T_2	T_2	A_1	0	0	0	1/3	0	
T_2	T_2	E	0	0	0	* 1/3	0	
T_2	A_2	T_1	0	1+	1+	1/3	0	
A_2	A_2	A_1	1+	1+	0	1	0	
A_1	A_1	A_1	0	0	0	1	0	

[a] See footnote on Table 3.

The subduction coefficients used to calculate the magnitudes of the 3Γ symbols were obtained by projection of the complex octahedral bases for each quantization from integer and half-integer spherical harmonics up to $J = 7$ [11].

2.6. Comparison with Previous Coupling Definitions for Complex Sets

In an earlier paper the relationship of the present 3Γ symbols to the V coefficients of Griffith was defined [1]. Two phase factors, one absorbed into the V coefficient and the second into the accompanying reduced matrix element are now accommodated in the single phase factor in (6). In addition, the present direct projection of the complex octahedral function does not result in the same bases obtained using Griffith's transformation from the real form on T_1 and T_2 alone [5], the present 3Γ symbols do not coincide either in phase or magnitude with V coefficients.

The 3-l symbols defined by Harnung and Schaeffer display an algebra similar to that for 3Γ symbols with three phase differences [4],

a) The 3Γ symbols follow Condon and Shortley conventions while the 3-l symbols follow the Racah convention. This imposes a modulus 4 on $(l_1 + l_2 + l_3)$ since $(i^4 = 1)$
b) An extra factor i is introduced in defining the antisymmetric combination M_s.
c) No phase factor is defined between coupling coefficients and 3-l symbols. The third factor means the 3-l symbols require special ordering of components in order to relate them to conventional 3-j (and hence the present 3Γ) symbols.

References

1. Hollebone, B. R., Donini, J. C.: Theoret. Chim. Acta. (Berl.) In Press
2. Hempel, J. C., Donini, J. C., Hollebone, B. R., Lever, A. B. P.: J. Am. Chem. Soc. **96**, 1693 (1974)
3. Ballhausen, C. J.: Introduction to ligand field theory, p. 61. New York: McGraw-Hill 1962
4. Harnung, S. E., Schaffer, C. E.: Struct. Bonding **12**, 201 (1972)
5. Griffith, J. S.: The irreducible tensor method for molecular symmetry groups. Englewood Cliffs, N.J.: Prentice-Hall 1962
6. Sugano, S., Tanabe, Y., Kamimura, H.: Multiplets of transition metal ions in crystals. New York: Academic Press 1970
7. Hollebone, B. R., Lever, A. B. P., Donini, J. C.: Mol. Phys. **22**, 155 (1971)
8. Wigner, E. P.: Quantum theory of angular momentum, Biedenharn, L. C., Van Dam, H., Eds., pp. 80, 89. New York: Academic Press 1965
9. Matsen, F. A., Plummer, O. R.: Group theory and its applications, Loebe, E. M., Ed., Vol. 1, p. 221. New York: Academic Press 1968
10. Dobosh, P.: Phys. Rev. **A5**, 2376 (1972)
11. Donini, J. C., Hollebone, B. R.: Unplublished. Tables of subduction coefficients are available from authors

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