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Original Investigations

Symmetry Adaption

II. Representations on Symmetric Polyhedra

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Stimulated by the invention of an algebraic formula for the coefficients of symmetry-adapted linear combinations in a previous paper [1], the representations induced by the edge vectors of a symmetric, molecular polyhedron $A_mB_nC_p$... are studied in detail. The following objects are defined (in brackets the analogous, common objects): Complete systems of standard functions (spherical harmonics), polyhedral vector coupling coefficients (3jm-symbols), polyhedral Racah coefficients (6j-symbols), polyhedral isoscalar factors (isoscalar factors). The algebraic properties and evaluation methods of these coefficients are discussed in order to be used in subsequent papers on quantities depending on symmetry-adapted orbitals and symmetry coordinates.

Key words: Symmetry-adaption – Racah algebra – Coordination polyhedra

1. Introduction

In a previous paper [1], in the following quoted by I, the construction of SALC's (symmetry-adapted linear combinations) was described. A central point was the reduction of the symmetry-group-representation induced by the change-of-position matrices (I, Eq. (2)). Since the multicenter integrals in symmetric molecules depend on all the edge vectors of the molecular polyhedron, it will be advisable to study the representations induced by all the edge vectors in this polyhedron. The position vectors of the atoms are special cases of edge vectors. In this paper we will elaborate the mathematical details of these representations, their decomposition into irreducible representations, and a certain, "triangular" direct product. In subsequent papers [2] this theory is applied to the diagonalization of molecular matrices.

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2. Representations on Polyhedral Edges

We study a symmetric molecule $A_mB_nC_p\ldots$ with several sets of symmetrically equivalent atoms. The edge vectors in this polyhedral framework are denoted by $\boldsymbol{S}_l$, $\boldsymbol{T}_m$ etc., where S, T, ... give the set of symmetrically equivalent edges, i.e. the edges, which are transferable into each other by the symmetry operations g of the symmetry group G. The indices numerate the edge vectors within an equivalent set. It will be necessary to distinguish carefully between parallel and antiparallel edge vectors. Especially the edge vectors between equivalent positions A_i and A_k will be counted twice: $\boldsymbol{S}_l = \boldsymbol{A}_i - \boldsymbol{A}_k$ and $\boldsymbol{S}_m = \boldsymbol{A}_k - \boldsymbol{A}_i$. Since atomic orbitals can be centered at different positions, but also at the same one, we will accept the null vector as a special edge too. Thus in the tetrahedron of CH_4 there are seventeen edge vectors: the null vector, the four vectors between C and H, and twelve (!) vectors between the H-atoms.

Each set S of equivalent edges induces a change-of-position representation σ^S of the symmetry group G:

$$g\boldsymbol{S}_l = \sum_m \sigma^S_{lm}(g)\boldsymbol{S}_m, \qquad g^{-1}\boldsymbol{S}_l = \sum_m \sigma^S_{ml}(g)\boldsymbol{S}_m \tag{1}$$

The characters

$$\sigma^S(g) = \sum_i \sigma^S_{ii}(g) \tag{2}$$

are equal to the number of edge vectors invariant under the operation g. We note the following property of the matrices $\sigma^S_{ik}(g)$:

$$\sigma^S_{lm}(gh) = \sigma^S_{lm}(g) \quad \text{when} \quad h\boldsymbol{S}_m = \boldsymbol{S}_m \tag{3}$$

With regard to potentials, multi-center integrals and other functions of the edge vectors we introduce the finite-dimensional, unitary space of functions over the discrete set $\mathscr{S} = \{\boldsymbol{S}_l\}$. In contrast to the Dirac brackets $\langle \boldsymbol{r} \mid G \rangle$ for the functions over the Euclidean space $\mathscr{E} = \{\boldsymbol{r}\}$ we use round brackets $(\boldsymbol{S}_l \mid G)$ for the functions over $\mathscr{S}$. The unitary space then is defined by

$$\mathscr{U} = \{(\boldsymbol{S}_l \mid G) \quad \text{with} \quad \boldsymbol{S}_l \in \mathscr{S}\}$$

and attached with the scalar product

$$(G|F) = \sum_l (G \mid \boldsymbol{S}_l)(\boldsymbol{S}_l \mid F) \tag{4}$$

σ^S now may be regarded as the representation of the group G in the space $\mathscr{U}$:

$$(g^{-1}\boldsymbol{S}_l \mid G) = \sum_m \sigma^S_{ml}(g)(\boldsymbol{S}_m \mid G) \tag{5}$$

The reduction of the reducible representation σ^S is equivalent to the search for the invariant subspaces of $\mathscr{U}$. The quintessence of paper I is, that a s.a. (symmetry-adapted) basis in $\mathscr{U}$ can be constructed with the aid of the s.a. functions over $\mathscr{E}$ centered at the centre of the polyhedron. We start with a given set of such functions

$\langle r|\alpha a s\rangle$, which are transformed according to the irreducible representation a (component s):

$$\langle g^{-1}\boldsymbol{r} \mid \alpha a s\rangle = \sum_t D^{a}_{ts}(g)\langle \boldsymbol{r} \mid \alpha a t\rangle \tag{6}$$

We need several, linearly independent functions for one a distinguished by α, because according to the character formula (I, Eq. (3))

$$n(a, S) = (1/\text{ord}\, G)\cdot \sum_C \lambda(C)\chi(a, C)^* \sigma^S(C)$$

the representation a may appear repeatedly in the reduction of σ^S. As in the appendix of I we will take into account the multiplicity $n(a, S) > 1$. In generalization of the normalized spherical harmonics of Eqs. (4) and (5) of I we set up the following orthonormalized set of standard functions (with respect to $\mathscr{U}$) or standard coefficients (as coefficients of an unitary transformation):

$$\text{Definition:}\quad (\boldsymbol{S}_l \mid S\beta a r) = \sum_\alpha d(S\beta a, \alpha)\langle \boldsymbol{S}_l \mid \alpha a r\rangle \tag{7}$$

where the coefficients $d(S\beta a, \alpha)$ are determined by

$$\sum_l (S\beta a r \mid \boldsymbol{S}_l)(\boldsymbol{S}_l \mid S\gamma a r) = \sum_{\alpha\alpha'} d(S\beta a, \alpha)^* d(S\gamma a, \alpha')\langle \alpha a r \mid \boldsymbol{S}_l\rangle\langle \boldsymbol{S}_l \mid \alpha' a r\rangle = \delta(\beta, \gamma) \tag{8}$$

The range of α and β is defined by the multiplicity: $1 \leqslant \alpha, \beta \leqslant n(a, S)$. As in I $\langle \boldsymbol{S}_l \mid \alpha a r\rangle$ are the s.a. functions $\langle \boldsymbol{r} \mid \alpha a r\rangle$ over $\mathscr{E}$ taken at the special values $\boldsymbol{S}_l$. As usually for $n(a, S) > 1$ the coefficients $d(S\beta a, \alpha)$ are not determined uniquely by (8) and orthonormalized linear-combinations

$$(\boldsymbol{S}_l \mid S\beta a r)' = \sum_\gamma c_{\beta\gamma}(\boldsymbol{S}_l \mid S\gamma a r)$$

are equivalent to (7). The elimination of this arbitrariness will be handled in a further paper [6]. We arrange the following phase convention

$$(\boldsymbol{S}_l \mid S\alpha a r)^* = (\boldsymbol{S}_l \mid S\alpha a^+ r) \tag{9}$$

Here we stress strongly that against common usage we define the representation a^+ simply by $D^{(a+)}_{ik}(g) = [D^{a}_{ik}(g)]^*$ without any basis transformations. For details see the appendix. If condition (9) is not met by the functions $\langle \boldsymbol{r} \mid \alpha a r\rangle$, i.e. $\langle \boldsymbol{r} \mid \alpha a r\rangle = \varphi(\alpha a)\langle \boldsymbol{r} \mid \alpha a^+ r\rangle$, (9) requires: $d(S\beta a^+, \alpha) = d(S\beta a, \alpha)^* \cdot \varphi(\alpha a)$.

We now list the properties of the standard functions $(\boldsymbol{S}_l \mid S\alpha a r)$:

1) They are generated from the set of s.a. functions $\langle \boldsymbol{r} \mid \alpha a r\rangle$, added in most character tables [7], by (7) and (8).
2) They have the orthogonality relations:

$$\sum_l (S\alpha a r \mid \boldsymbol{S}_l)(\boldsymbol{S}_l \mid S\beta \ell s) = \delta(\alpha, \beta)\delta(a, \ell)\delta(r, s) \tag{10}$$

$$\sum_{\alpha a r} (\boldsymbol{S}_l \mid S\alpha a r)(S\alpha a r \mid \boldsymbol{S}_m) = \delta(l, m) \tag{11}$$

(proof given below)

3) Because of 2) they form a complete basis in $\mathscr{U}$, thus for every $(\boldsymbol{S}_l \mid G) \in \mathscr{U}$:

$$(\boldsymbol{S}_l \mid G) = \sum_{\alpha a r} (\boldsymbol{S}_l \mid S\alpha a r)(S\alpha a r \mid G)$$

with $$(S\alpha a r \mid G) = \sum_l (S\alpha a r \mid \boldsymbol{S}_l)(\boldsymbol{S}_l \mid G)$$

Similar expansions hold for functions of several edge vectors, which will be important for instance for multi-center integrals. A case of special interest are s.a. spherical harmonics $\langle \boldsymbol{r} \mid L\alpha a r\rangle$ taken at $\boldsymbol{r} = \boldsymbol{S}_l$:

$$\langle \boldsymbol{S}_l \mid L\alpha a r\rangle = \sum_\beta c(S\beta a, L\alpha)(\boldsymbol{S}_l \mid S\beta a r) \tag{12}$$

where the coefficients $c(S\beta a, L\alpha)$ can be calculated from known quantities:

$$c(S\beta a, L\alpha) = \sum_l (S\beta a r \mid \boldsymbol{S}_l)\langle \boldsymbol{S}_l \mid L\alpha a r\rangle \tag{13}$$

4) They form a unitary matrix, which reduces σ^s (proof given below).
5) Likewise they are the coefficients of the SALC's built up from $A_{(1g)}$-orbitals (if $\boldsymbol{S}_l$ are position vectors):

$$\langle \boldsymbol{r} \mid \alpha a r\rangle = \sum_l (\boldsymbol{S}_l \mid S\alpha a r)\langle \boldsymbol{r} - \boldsymbol{S}_l \mid A_{(1g)} 0\rangle$$

(generalization Eq. (18) below)

We first prove point 4): From (5) follows

$$(g^{-1}\boldsymbol{S}_l \mid S\alpha a r) = \sum_m \sigma^s_{ml}(g)(\boldsymbol{S}_m \mid S\alpha a r)$$

and on the other hand from (6) and (7)

$$(g^{-1}\boldsymbol{S}_l \mid S\beta a r) = \sum_{\alpha t} D^a_{tr}(g) d(S\beta a, \alpha)\langle \boldsymbol{S}_l \mid \alpha a t\rangle = \sum_t D^a_{tr}(g)(\boldsymbol{S}_l \mid S\beta a t), \tag{14}$$

so that with (8):

$$\sum_{lm} (S\gamma a t \mid \boldsymbol{S}_l)\sigma^S_{ml}(g)(\boldsymbol{S}_m \mid S\beta a r) = D^a_{tr}(g)\delta(\beta, \gamma),$$

what was to be proved.

It is easy to point out the generalization (10) of (8) by replacing $\boldsymbol{S}_l$ by $g^{-1}\boldsymbol{S}_l$ on the left hand side, using (14) and summing over all $g \in G$. In order to prove (11), we abbreviate the left side of (11) by X_{lm}. Now we have $\sum_l X_{ll} = n(a, S) \cdot \dim a = Z(S)$, the number of the edge vectors in set $\mathscr{S}$. By the aid of $g\boldsymbol{S}_k = \boldsymbol{S}_l$ one sees $X_{ll} = X_{kk}$, so that $X_{ll} = 1$. With (8) one gets $\sum_m X_{lm} X_{ml} = X_{ll} = 1$, i.e. $\sum_{m \neq l} |X_{lm}|^2 = 0$, so that $X_{lm} = 0$ for $m \neq 1$.

With the standard functions $(\boldsymbol{S}_l \mid S\alpha a r)$ it is possible to generalize the SALC coefficients of Eqs. (10) and (24) of I for arbitrary edges:

$$K(\gamma c p, Sj\alpha a, br) = \sum_m \langle am, br \mid \gamma c p\rangle(\boldsymbol{S}_j \mid S\alpha a m) \tag{15}$$

As in Eq. (24) of I γ takes account of the multiplicity of c in the direct product $a \times b$. Because of the orthogonality relations (10) and (11) and those of the Clebsch–Gordan coefficients, the SALC coefficients have orthogonality relations too:

$$\sum_{jr} K(\gamma c p,\, Sj\alpha a,\, br)\cdot K(\gamma' c' p',\, Sj\alpha' a',\, br) = \delta(\gamma,\gamma')\delta(c,c')\delta(p,p')\delta(\alpha,\alpha')\delta(a,a') \tag{16}$$

$$\sum_{\alpha a}\sum_{\gamma c p} K(\gamma c p,\, Sj\alpha a,\, br)\cdot K(\gamma c p,\, Sk\alpha a,\, bs) = \delta(j,k)\delta(r,s) \tag{17}$$

This guarantees the symmetry adaption being a unitary transformation. If the edge vectors are selected to be the position vectors of an equivalent, atomic set A, then the s.a. MO's as in Eq. (11) or (24) of I:

$$|(A\alpha a,\, nl\beta b)\gamma c p\rangle = \sum_{jr} K(\gamma c p,\, Aj\alpha a,\, br)\cdot |Ajnl\beta b r\rangle \tag{18}$$

where the AO's defined by $\langle \boldsymbol{r} \mid Ajnl\beta b r\rangle = \langle \boldsymbol{r} - A_j \mid nl\beta b r\rangle$ are already s.a. and connected with the AO's $|nlm\rangle$, classified according to the angular momentum by

$$|nl\beta b r\rangle = \sum_m \langle lm \mid l\beta b r\rangle \cdot |nlm\rangle. \tag{19}$$

We insert this into (18) in order to have a general SALC formula with respect to the angular momentum quantum numbers:

$$|(A\alpha a,\, nl\beta b)\gamma c p\rangle = \sum_{jm} M(\gamma c p,\, Aj\alpha a,\, (\beta b)lm)\cdot |Ajnlm\rangle \tag{20}$$

with

$$M(\gamma c p,\, Aj\alpha a,\, (\beta b)lm) = \sum_r K(\gamma c p,\, Aj\alpha a,\, br)\langle lm \mid l\beta b r\rangle \tag{21}$$

The orthogonality relations of the M-coefficients are:

$$\sum_{jm} M(\gamma c p,\, Aj\alpha a,\, (\beta b)lm)\cdot M(\gamma' c' p',\, Aj\alpha' a',\, (\beta' b')lm) = \delta(\gamma,\gamma')\delta(c,c')\delta(p,p')\delta(\alpha,\alpha')\delta(a,a')\delta(\beta,\beta')\delta(b,b') \tag{22}$$

$$\sum_{\alpha a \beta b}\sum_{\gamma c p} M(\gamma c p,\, Aj\alpha a,\, (\beta b)lm)\cdot M(\gamma c p,\, Ak\alpha a,\, (\beta b)ln) = \delta(j,k)\delta(m,n) \tag{23}$$

The SALC coefficients with respect to general edge vectors can serve to build up s.a. two-electron functions or electron-hole functions in the sense of the VB theory. Before doing so in Eq. (39) we need some algebraic preparation given in the next section.

In many books the numerical values of the coefficients defined by (7), (15) and (21) are calculated by the projection-operator technique or a related one. It may therefore be advisable to stop a moment to point out the significance of our formulae: Since (7), (15) and (21) are a specification and generalization of I, they, of course, can serve for the calculation of SALC's for polyhedra not yet elaborated. But our interest now exceeds this direct application.

Just as in the case of Clebsch–Gordan coefficients extensive numerical tabulation does not make obsolete algebraic formulae. On the contrary in the author's opinion only the latter show command over the matter. In consequent tensor algebraic calculation the basic, but coordinate-dependent Clebsch–Gordan coefficients are eliminated in favour of invariants like Racah coefficients or reduced matrix elements etc. In the same sense our formulae will make it possible to dissolve the SALC coefficients (21) in favour of invariants to be defined below. First applications will follow in subsequent papers [2]. The ultimate desideratum, of course, is the calculation of energies etc. using no coordinate- or numeration-dependent quantities, but only invariants.

3. Racah Algebra on Coordination Polyhedra

In order to formulate s.a. objects with respect to several atoms or edges it is suitable to number the symmetrically equivalent triangles with the edges S, T and U as $STUi$ or shortly Δi. We define the following triangular matrices:

$$PV\begin{pmatrix}\Delta & S & T & U\\ i & m & n & p\end{pmatrix}=\begin{cases}1 & \text{when } \boldsymbol{S}_m+\boldsymbol{T}_n+\boldsymbol{U}_p=0 \quad \text{and} \quad \boldsymbol{S}_m,\ \boldsymbol{T}_n,\ \boldsymbol{U}_p \text{ are edges of } \Delta i\\ 0 & \text{otherwise}\end{cases} \tag{24}$$

The nomenclature PV will become clear below. We choose PV totally symmetric in S, T and U. Because $-\boldsymbol{S}_m$, $-\boldsymbol{T}_n$ and $-\boldsymbol{U}_p$ form the same triangle with inverted sense of rotation, we define

$$PV\begin{pmatrix}-\Delta & -S & -T & -U\\ i & m & n & p\end{pmatrix}=PV\begin{pmatrix}\Delta & S & T & U\\ i & m & n & p\end{pmatrix} \tag{25}$$

One easily verifies the othogonality relations:

$$\sum_i PV\begin{pmatrix}-\Delta & -S & -T & -U\\ i & m & n & p\end{pmatrix}PV\begin{pmatrix}\Delta & S & T & U\\ i & k & l & q\end{pmatrix}=\delta(m,k)\delta(n,1)\delta(p,q)\delta(\Delta,STU) \tag{26}$$

$$\sum_{mnp} PV\begin{pmatrix}\Delta & -S & -T & -U\\ i & m & n & p\end{pmatrix}PV\begin{pmatrix}\Delta' & S & T & U\\ k & m & n & p\end{pmatrix}=\delta(\Delta,\Delta')\delta(i,k)\delta(\Delta,STU) \tag{27}$$

The triangles Δi of course induce a representation $\sigma\Delta$ on their part:

$$g(\Delta i)=\sum_k \sigma^{\Delta}_{ik}(g)(\Delta k) \tag{28}$$

Therefore simultaneous operation of g on Δi, $\boldsymbol{S}_l$, $\boldsymbol{T}_m$ and $\boldsymbol{U}_n$ gives:

$$\sum_{ilmn} \sigma^{\Delta}_{ji}(g)\sigma^{S}_{pl}(g)\sigma^{T}_{qm}(g)\sigma^{U}_{rn}(g)PV\begin{pmatrix}\Delta & S & T & U\\ i & l & m & n\end{pmatrix}=PV\begin{pmatrix}\Delta & S & T & U\\ j & p & q & r\end{pmatrix} \tag{29}$$

Some reordering gives with (27):

$$\sum_{lmn}\sum_{pqr} PV\begin{pmatrix}-\Delta & -S & -T & -U\\ j & p & q & r\end{pmatrix}\sigma^{S}_{pl}(g)\sigma^{T}_{qm}(g)\sigma^{U}_{rn}(g)PV\begin{pmatrix}\Delta & S & T & U\\ i & l & m & n\end{pmatrix}$$
$$=\sigma^{\Delta}_{ji}(g)\delta(\Delta,STU) \tag{30}$$

which shows that the triangular matrices couple the representations σ^S, σ^T and σ^U to give σ^{STU} quite as the ordinary vector coupling coefficients $V_\alpha\begin{pmatrix}a & b & c\\ i & k & l\end{pmatrix}$ couple $a\times b\times c$ to give $A_{(1g)}$. We therefore termed them PV, "polyhedral vector coupling coefficients". There is a difference of the indices i and α. Whereas α indicates the repeatedly occurring $A_{(1g)}$ in the direct triple product $a \times b \times c$, i is a component index of the multidimensional representation σ^{Δ}. Of course it is possible to interpret PV as a $4jm$-symbol [3], which couples four representations to give $A_{(1g)}$; but we shall not follow this way. As the reader will foresee, it is now possible to introduce Racah coefficients via the tetrahedra built up by four triangles, respectively spanned by the six edges $STUXYZ$. The symbolical, graphical interpretation of Racah coefficients [3] is here to be taken literally. These "polyhedral Racah coefficients" PW will carry four additional indices as in the theory of non-simply reducible groups [4]. In order to have correct triangular edge vector sums according to (24) we have to use some inverse edge vectors:

$$PW\begin{pmatrix} STU \\ XYZ \end{pmatrix}_{ijkl} = \sum_{mnp} \sum_{qrs} PV\begin{pmatrix} \Delta\ S - Y\ Z \\ i\ m\ \ n\ p \end{pmatrix} PV\begin{pmatrix} \Theta\ X\ T - Z \\ j\ q\ r\ \ p \end{pmatrix} PV\begin{pmatrix} \Lambda - X\ Y\ U \\ k\ \ q\ n\ s \end{pmatrix} PV\begin{pmatrix} \Gamma - S - T - U \\ l\ \ m\ \ r\ \ s \end{pmatrix} \quad (31)$$

We take for granted $\Delta = S - YZ$, $\Theta = XT - Z$, $\Lambda = -XYU$, $\Gamma = -S - T - U$ and omit their notation on the left hand side. The introduction of $-S$ etc. in (26) and (27) was somewhat artificial, but necessary in (31). We shall always arrange the summations to run over pairs $-Sn$ and Sn in analogy to the ordinary Racah algebra, where the summation always runs over an and a^+n, cf. [4] and the appendix. With (26) one obtains from (31) the well-known recoupling relations:

$$\sum_{l} PV\begin{pmatrix} -\Gamma\ S\ T\ U \\ l\ m\ r\ s \end{pmatrix} PW\begin{pmatrix} STU \\ XYZ \end{pmatrix}_{ijkl} = \sum_{npq} PV\begin{pmatrix} \Delta\ S - Y\ Z \\ i\ m\ \ n\ p \end{pmatrix} PV\begin{pmatrix} \Theta\ X\ T\ \ Z \\ j\ q\ r\ \ p \end{pmatrix} PV\begin{pmatrix} \Lambda - X\ Y\ U \\ k\ \ q\ n\ s \end{pmatrix} \quad (32)$$

$$\sum_{il} PV\begin{pmatrix} -\Delta - S\ Y - Z \\ i\ \ m\ n\ \ p' \end{pmatrix} PV\begin{pmatrix} -\Gamma\ S\ T\ U \\ l\ m\ r\ s \end{pmatrix} PW\begin{pmatrix} STU \\ XYZ \end{pmatrix}_{ijkl} = \sum_{q} PV\begin{pmatrix} \Theta\ X\ T - Z \\ j\ q\ r\ \ p \end{pmatrix} PV\begin{pmatrix} \Lambda - X\ Y\ U \\ k\ \ q\ n\ s \end{pmatrix} \delta(p, p') \quad (33)$$

By setting $p = p'$ and summation over m the last one is given a more familiar form except for the factor $Z(S)$:

$$\sum_{ilm} PV\begin{pmatrix} -\Delta - S\ Y - Z \\ i\ \ m\ n\ \ p \end{pmatrix} PV\begin{pmatrix} -\Gamma\ S\ T\ U \\ l\ m\ r\ s \end{pmatrix} PW\begin{pmatrix} STU \\ XYZ \end{pmatrix}_{ijkl} = \sum_{p} PV\begin{pmatrix} \Theta\ X\ T - Z \\ j\ q\ r\ \ p \end{pmatrix} PV\begin{pmatrix} \Lambda - X\ Y\ U \\ k\ \ q\ n\ s \end{pmatrix} Z(S) \quad (34)$$

When we need not distinguish the different triangle $STUi$, we can sum over i. This is equivalent to the reduction of $\sigma^{STU} \to A_{(1g)}$, the reduction coefficient being:

$$(STUi \mid STU\, A_{(1g)}) = Z(STU)^{-1/2} \quad (35)$$

where $Z(STU)$ is the number of equivalent triangles. Performing the summation we get a partly s.a. form of PV (the totally s.a. form is given below in (40)):

$$\tau\begin{pmatrix} S & T & U \\ m & n & p \end{pmatrix} = PV\begin{pmatrix} STU & S & T & U \\ A_{(1g)} & m & n & p \end{pmatrix} = \sum_i PV\begin{pmatrix} STU & S & T & U \\ i & m & n & p \end{pmatrix} (STUi \mid STU\, A_{(1g)}) \quad (36)$$

Here we have introduced the shorter notation with τ, because these coefficients will be of much use since they indicate whether or not three edges form a triangle:

$$\tau\begin{pmatrix} S & T & U \\ m & n & p \end{pmatrix} = \begin{cases} Z(STU)^{-1/2} & \text{when} \quad \boldsymbol{S}_m + \boldsymbol{T}_n + \boldsymbol{U}_p = \boldsymbol{0} \\ 0 & \text{otherwise} \end{cases} \quad (37)$$

The normalization of (35) and (36) is such that

$$\sum_{mnp} \tau\begin{pmatrix} S & T & U \\ m & n & p \end{pmatrix} \tau\begin{pmatrix} -S & -T & -U \\ m & n & p \end{pmatrix} = 1$$

and

$$\sum_{np} \tau\begin{pmatrix} S & T & U \\ m & n & p \end{pmatrix} \tau\begin{pmatrix} -R & -T & -U \\ q & n & p \end{pmatrix} = \delta(R, S)\delta(m, q)/Z(S). \quad (38)$$

When $g\boldsymbol{S}_m = \boldsymbol{S}_m$ but $g\boldsymbol{T}_n \neq \boldsymbol{T}_n$, there are several triangles STU having one S-edge in common:

$$\tau\begin{pmatrix} S & T & U \\ m & n & p \end{pmatrix} = \tau\begin{pmatrix} S & gT & gU \\ m & n & p \end{pmatrix}$$

Because of this ambiguity there is in general no simple orthogonality relation involving a sum over Sm as for the vector coupling coefficients. This is the reason why we had to start with the PV coefficients and not the simpler τ.

As a first application of τ we are now prepared to write down the above announced, s.a. two-electron functions using an anti-symmetrization operator $\mathscr{A}$:

$$\langle \boldsymbol{r}_1, \boldsymbol{r}_2 \mid (Anl, Bn'l')(S\alpha a, L\beta b)\gamma c p\rangle = \sum_{jLM} M(\gamma c p, Sj\alpha a, (\beta b)LM) \cdot \sum_{ikmm'} \tau\begin{pmatrix} -A & B & S \\ i & k & j \end{pmatrix} \langle lm, l'm' \mid LM\rangle \cdot \mathscr{A}\langle \boldsymbol{r}_1 \mid Ainlm\rangle \langle \boldsymbol{r}_2 \mid Bkn'l'm'\rangle \quad (39)$$

We note that (39) in the case of $A = B$ shows the necessity to distinguish the edge vectors $\boldsymbol{A}_i - \boldsymbol{A}_k$ from $\boldsymbol{A}_k - \boldsymbol{A}_i$ as a different $\boldsymbol{S}_j$.

Since the representations σ^S, σ^T etc. form a closed system of reducible representations of the group G, they are in analogy to the representations of a larger group $H \supset G$, which form a closed system of reducible representations of G too. But the following is no group chain calculation, because the σ representations are not irreducible with respect to a common supergroup. In consequence of the analogy we also can take over the important concept of isoscalar factors connecting the

PV coefficients with the ordinary V coefficients. To this end we transform the coefficients defined in (36), which couple $\sigma^S \times \sigma^T \times \sigma^U \rightarrow A_{(1g)}$, into the s.a. basis using the standard functions (7):

$$\tau\begin{pmatrix} S & T & U \\ \alpha a p & \beta b q & \gamma c r \end{pmatrix} = \sum_{ikl} \tau\begin{pmatrix} S & T & U \\ i & k & l \end{pmatrix} (\boldsymbol{S}_i \mid S\alpha a p)(\boldsymbol{T}_k \mid T\beta b q)(\boldsymbol{U}_l \mid U\gamma c r) \tag{40}$$

where we have used (25). One now makes sure that (40) transforms according to the direct product $a \times b \times c$. Using the Wigner–Eckart theorem one is led to the analogue of Racahs factorization lemma [5], the reduced matrix elements being the polyhedral isoscalar factors PIs:

$$\tau\begin{pmatrix} S & T & U \\ \alpha a p & \beta b q & \gamma c r \end{pmatrix} = \sum_{\varepsilon} PIs_{\varepsilon}\begin{pmatrix} S & T & U \\ \alpha a & \beta b & \gamma c \end{pmatrix} V_{\varepsilon}\begin{pmatrix} a & b & c \\ p & q & r \end{pmatrix} \tag{41}$$

The sum over ε, of course, only occurs in non-simply reducible groups. The PIs can be calculated by solving (41) and inserting it into (40):

$$PIs_{\varepsilon}\begin{pmatrix} S & T & U \\ \alpha a & \beta b & \gamma c \end{pmatrix} = \sum_{pqr} \sum_{ikl} \tau\begin{pmatrix} S & T & U \\ i & k & l \end{pmatrix} (\boldsymbol{S}_i \mid S\alpha a p)(\boldsymbol{T}_k \mid T\beta b q)(\boldsymbol{U}_l \mid U\gamma c r) V_{\varepsilon}\begin{pmatrix} abc \\ pqr \end{pmatrix} \tag{42}$$

where τ can be taken from (37).

The significance of (42) becomes clear from the fact that the standard functions occur in the SALC coefficients and therefore are involved in the integrals of s.a. LCAO's. We now are able to evaluate triangular products of standard functions and moreover because of the expansion (12) all triangular products of spherical harmonics with edge vectors as arguments.

A further class of coefficients needed in MO calculations is the sum over the product of three standard functions of one set of equivalent edges. These coefficients are analogous to the integral over three spherical harmonics. Because of the completeness of standard functions a product $(\boldsymbol{S}_1 \mid S\beta b q)(\boldsymbol{S}_l \mid S\gamma c r)$ must be expandable in the same set of standard functions:

$$(\boldsymbol{S}_l \mid S\beta b q)(\boldsymbol{S}_l \mid S\gamma c r) = \sum_{\alpha a p} f(S, \alpha a p, \beta b q, \gamma c r)(\boldsymbol{S}_l \mid S\alpha a p)$$

As one easily sees f has the property of a tensor product and therefore can be factorized according to the Wigner–Eckart theorem:

$$(\boldsymbol{S}_l \mid S\beta b q)(\boldsymbol{S}_l \mid S\gamma c r) = \sum_{\varepsilon \alpha a p} P_{\varepsilon}(S, \alpha a \| \beta b \| \gamma c) V_{\varepsilon}\begin{pmatrix} a^+ & b & c \\ p & q & r \end{pmatrix} (\boldsymbol{S}_l \mid S\alpha a p) \tag{43}$$

Of course the reduced, "polyhedral matrix element" P_{ε} can be calculated by:

$$P_{\varepsilon}(S, \alpha a \| \beta b \| \gamma c) = \sum_{lpqr} (S\alpha a p \mid \boldsymbol{S}_l)(\boldsymbol{S}_l \mid S\beta b q)(\boldsymbol{S}_l \mid S\gamma c r) V_{\varepsilon}\begin{pmatrix} a^+ & b & c \\ p & q & r \end{pmatrix} \tag{44}$$

The applications will show that a consequent tensor algebraic calculation of physical quantities contains the invariants PIs, P and c only.

4. Special Cases and Sum Rules

Two simple, special cases can be evaluated immediately. From (42) follows (we abbreviate $A_{(1g)}=o$):

$$PIs\begin{pmatrix} -A & O & B \\ \alpha a^+ & o & \beta b \end{pmatrix} = \delta(A, B)\delta(a, b)\delta(\alpha, \beta)\cdot(\dim a/Z(A))^{1/2} \tag{45}$$

and from (44):

$$P(S, \alpha a\|o\|\gamma c) = \delta(a, c)\delta(\alpha, \gamma)\cdot(\dim a/Z(S))^{1/2} \tag{46}$$

The τ-coefficients of Eq. (37) have the following sum rule, which is in analogy to one of the ordinary V-coefficients [9]:

$$\sum_k \tau\begin{pmatrix} -A & A & S \\ k & k & l \end{pmatrix} = Z(A)^{1/2}\delta(S, 0)\delta(l, 0) \tag{47}$$

From this follows a sum rule of the polyhedral isoscalars:

$$\sum_{\alpha a} (\dim a)^{1/2} PIs\begin{pmatrix} -A & A & S \\ \alpha a^+ & \alpha a & o \end{pmatrix} = Z(A)^{1/2}\delta(S, 0) \tag{48}$$

Finally there is an orthogonality relation quite analogously to the ordinary isoscalars [5]. The substitution of (41) into (38) yields:

$$\sum_{\varepsilon\beta}\sum_{b\gamma c} PIs^*_\varepsilon\begin{pmatrix} S & T & U \\ \alpha a & \beta b & \gamma c \end{pmatrix} PIs_\varepsilon\begin{pmatrix} R & T & U \\ \delta a & \beta b & \gamma c \end{pmatrix} = \delta(R, S)\delta(\alpha, \delta)\cdot\dim a/Z(S) \tag{49}$$

But there will be no simple analogue of the second orthogonality relation because of the lack of such a second relation for the τ coefficients.

5. Appendix on Nomenclature

Since there are so many different conventions in the Racah algebra, we should state our notation in this and the subsequent papers. In principle we keep to the enlightening synopsis of Butler [4], making only marginal changes. Butler's notation is very rich in indices, so that indices of indices are frequent. On the other hand the two-line notation of $3j$- and $6j$-symbols is well established by the work of Wigner. Following the work of Griffith [9] it is convenient to distinguish the corresponding properties of point groups by prefixes. These are: V for the $3jm$-symbols, W for the $6j$-symbols and Is for isoscalar factors. Consequently we have termed the polyhedral coefficients PV, PW, and PIs.

As for the conjugation of a representation a there is to say the following. In the cited article of Butler occurs the usual notation a^*, for instance in

$$V_\varepsilon\begin{pmatrix} a^* & b & c \\ i & k & l \end{pmatrix} = (a^* b c)_{\varepsilon ikl}, \tag{50}$$

where $\mathscr{a}^*$ is defined not only by the conjugation but also by an additional basis transformation (again $\mathscr{o}=A_{(1g)}$):

$$D_{ik}^{(\mathscr{a}^*)}(g)=\sum_{lm} V\begin{pmatrix} \mathscr{o} & \mathscr{a} & \mathscr{a}^* \\ o & m & i \end{pmatrix} \dim \mathscr{a}^{1/2}[D_{ml}^{\mathscr{a}}(g)]^* \dim \mathscr{a}^{1/2}\, V\begin{pmatrix} \mathscr{o} & \mathscr{a} & \mathscr{a}^* \\ o & l & k \end{pmatrix}$$

Consequently the coefficients

$$\dim \mathscr{a}^{1/2}\, V\begin{pmatrix} \mathscr{o} & \mathscr{a} & \mathscr{a}^* \\ o & m & i \end{pmatrix}$$

must always be carried along when a conjugation is needed. But Butler also has introduced a more elegant version, which we indicate by $\mathscr{a}^+$:

$$V_\varepsilon\begin{pmatrix} \mathscr{a}^+ & \mathscr{b} & \mathscr{c} \\ i & k & l \end{pmatrix}=(\mathscr{a}\mathscr{b}\mathscr{c})_{\varepsilon^i kl}$$

The position of the indices in Butler's notation on the right side can only be understood with reference to $(\mathscr{a}\mathscr{b}\mathscr{c})_{\varepsilon ikl}$ and does not express that $\mathscr{a}^+$ is an representation of its own right with matrices

$$D_{ik}^{(\mathscr{a}^+)}(g)=[D_{ik}^{\mathscr{a}}(g)]^* \tag{51}$$

and basis functions

$$\langle \boldsymbol{r} \mid \mathscr{a}^+ m\rangle=\langle \boldsymbol{r} \mid \mathscr{a} m\rangle^*=\langle \mathscr{a} m \mid \boldsymbol{r}\rangle \tag{52}$$

So we regard (50) as the primal coefficient and get much simpler expressions. The whole machinery works without consideration, whether $\mathscr{a}^+$ is equivalent to $\mathscr{a}$ or not. Butler's theorem on conjugation reads:

$$V_\varepsilon^*\begin{pmatrix} \mathscr{a} & \mathscr{b} & \mathscr{c} \\ i & k & l \end{pmatrix}=V_\varepsilon\begin{pmatrix} \mathscr{a}^+ & \mathscr{b}^+ & \mathscr{c}^+ \\ i & k & l \end{pmatrix} \tag{53}$$

From this follows:

$$Is_\varepsilon^*\begin{pmatrix} j & k & l \\ \alpha\mathscr{a} & \beta\mathscr{b} & \gamma\mathscr{c} \end{pmatrix}=Is_\varepsilon\begin{pmatrix} j^+ & k^+ & l^+ \\ \alpha\mathscr{a}^+ & \beta\mathscr{b}^+ & \gamma\mathscr{c}^+ \end{pmatrix}, \qquad PIs_\varepsilon^*\begin{pmatrix} A & B & C \\ \alpha\mathscr{a} & \beta\mathscr{b} & \gamma\mathscr{c} \end{pmatrix}= PIs_\varepsilon\begin{pmatrix} A & B & C \\ \alpha\mathscr{a}^+ & \beta\mathscr{b}^+ & \gamma\mathscr{c}^+ \end{pmatrix} \tag{54}$$

The 6*j*-symbol is:

$$W\begin{pmatrix} \mathscr{a} & \mathscr{b} & \mathscr{c} \\ \mathscr{d} & \mathscr{e} & \mathscr{f} \end{pmatrix}_{\alpha\beta\gamma\delta}=\sum_{ijk}\sum_{lmn} V_\alpha\begin{pmatrix} \mathscr{a} & \mathscr{e}^+ & \mathscr{f} \\ i & l & m \end{pmatrix} V_\beta\begin{pmatrix} \mathscr{d} & \mathscr{b} & \mathscr{f}^+ \\ n & j & m \end{pmatrix} V_\gamma\begin{pmatrix} \mathscr{d}^+ & \mathscr{e} & \mathscr{c} \\ n & l & k \end{pmatrix} V_\delta\begin{pmatrix} \mathscr{a}^+ & \mathscr{b}^+ & \mathscr{c}^+ \\ i & j & k \end{pmatrix} \tag{55}$$

This version is the godfather of our definition of the polyhedral Racah coefficient in (31). As in (55) correct sums only can run over pairs of $\mathscr{a}i$ and $\mathscr{a}^+i$. From (50) follows:

$$V\begin{pmatrix} \mathscr{o} & \mathscr{a} & \mathscr{b}^+ \\ o & i & k \end{pmatrix}=\delta(\mathscr{a},\mathscr{b})\delta(i,k)\cdot\dim \mathscr{a}^{1/2} \tag{56}$$

Since there is no phase factor in this relation, none occurs in Eq. (48). All this is more complicated if a^* is used.

As for the Clebsch–Gordan coefficients occurring in the SALC coefficients (15) and (21) we have the connection:

$$\langle \gamma c p \mid a m, b n\rangle = \dim c^{1/2} K_\gamma(abc) V_\gamma\begin{pmatrix} a b c^+ \\ m n p \end{pmatrix} \tag{57}$$

According to the sensible phase condition of Butler we choose $K_\gamma(abc)=1$ for the point groups, but for $SU(2)$ $K(jkl)=(-1)^{j-k+l}$ in accordance with Condon and Shortley.

Since for the group $SU(2)$ the $3jm$-symbols are well established with other conventions, we give the following relation:

$$\begin{pmatrix} j^+ & k & l \\ m & n & p \end{pmatrix} = (-1)^{j-m}\begin{pmatrix} j & k & l \\ -m & n & p \end{pmatrix} \tag{58}$$

It is usual to use the same symbol V for the coefficients in different bases, i.e.

$$V\begin{pmatrix} a & b & c \\ i & k & l \end{pmatrix} \quad \text{and in a subgroup basis} \quad V\begin{pmatrix} a & b & c \\ \alpha a' r & \beta b' s & \gamma c' t \end{pmatrix}.$$

In this sense we have used the same symbol PV in (24) and (36) and likewise the same τ in (36) or (37) and (40).

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