Theoret. Chim. Acta (Berl.) 37, 233—250 (1975)

The Coupling Algebra of Trigonally Subduced Crystal Field Eigenvectors

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Received September 27, 1974

The general theory of subduction of eigenvectors between infinite groups is used to derive a finite group subduction operator and define the corresponding subduction coefficients. The coupling behaviour of these subduced eigenvectors can then be described in terms of 3Γ symbols. These symbols, defined only in relation to complex basis sets are all fully real and have all phases fixed by the subduction operator. They differ from V coefficients in two phase relationships and have the advantage, unlike V coefficients, of retaining all the symmetry properties and selection rules of Wigner 3-j symbols. Appropriate label systems which render these properties in terms of simple algebras are given for all quantizing axes available in O_h. The specific set of 3Γ symbols for each quantization is determined by the orientation of the coordinate axes in the Hamiltonian. The four possible orientations for trigonal quantization are examined and the operator chosen which produces eigenvectors with conventional conjugate phases and a fully real set of 3Γ symbols.

Key word: Crystal field theory

1. Introduction

The analysis of the physical properties of trigonally coordinated metal ions has been a source of difficulty for many years [1]. In contrast to the treatments of the more fully understood tetragonal [2] and digonal [3] quantizations, there still are substantial differences of opinion concerning the parametrization of trigonal groups, the nature of the eigenvector couplings and their phase relationships and the correspondence of various trigonal subgroups with each other.

In attempting to formulate both an Hermitian Normalized Spherical Harmonic Hamiltonian [3] which can be subjected to subduction into trigonal subgroups and also in trying to establish component symbols and their algebra of coupling, it was found necessary to formulate a more general theory of both subduction of eigenvectors into subgroups and transduction into isomorphic groups. This general theory for finite groups can be derived as corollaries of well established theorems applicable to continuous groups [4]. By substitution of the appropriate modulus of the finite quantizing axis any subduction chain [5] can be examined, the component symbols derived and the Hermitian operator generated [6]. The derivation of subduction coefficients by standard symmetry adaptation techniques becomes progressively more difficult with increasing order of the spherical harmonics. Computer diagonalization methods also quickly reach their limits of precision. An alternative method of deriving these wave functions

is available if some subduction coefficients for the lowest values of l are known. These coefficients may be substituted into the subduction equation defining the coupling coefficients of the finite group which are themselves independent of l. Using the triangular rules in the subduced 3-j symbols, the symmetry adaptation can be extended indefinitely with no ambiguities.

In order to use this technique however the appropriate set of coupling symbols in the finite group must be available. Present tabulations for complex trigonal bases cannot be used because the phase conventions were chosen without reference to 3-j symbols and with unconventional conjugation.

Thus in this paper the subduction operators are used to symmetry adapt the first four sets of spherical harmonics to a conventional choice of coordinates. These eigenvectors are then used to define the desired set of coupling symbols which mimic the 3-j symbols and these in turn are used to extend the set of symmetry adapted eigenvectors up to $l=6$. This process guarantees Hermitian matrices and permits the abstraction of chemical and geometric information from the spectral parameters described in the next paper.

2. General Theory of Subduction

The starting point for a general theory of subduction in finite groups can be taken from the branching rules used to subduce continuous groups. Since the theory of continuous groups developed by Lie and Weyl is a generalization of finite group theory [4], a finite group subduction theory can be constructed as corollaries for special conditions of the general theorems of continuous groups.

This theory is constructed upon the behaviour of Casimir's operator

$$\hat{G}=g^{\varrho\sigma}\hat{X}_{\varrho}\hat{X}_{\sigma} \tag{1}$$

which is a product of infinitesimal tensor operators and commutes with all other operators including the Hamiltonian X_J of the group. In the three-dimensional rotation group R_3 it becomes $\hat{L}^2$. Since subduction from R_3 to finite groups concerns only orbital behaviour it will mimic the branching between groups $R_{(2l+1)}$ for which Casimir's operator can be written;

$$\begin{aligned}\hat{G}(R_{2l+1}) &= 1/4(2l-1)^{-1}\sum_{\nu\upsilon}\hat{W}_{\nu\upsilon}\hat{W}_{\upsilon\nu}\\ &= 1/4(2l-1)^{-1}\left\{\sum_{j}\hat{W}_{jj}^2+\sum_{\nu\neq\upsilon}\hat{W}_{\nu\upsilon}\hat{W}_{\upsilon\nu}\right\}.\end{aligned} \tag{2}$$

The eigenvalues of this operator like those of $\hat{L}^2$ in R_3 are sums of the effects of the commuting W_{jj}^2 and non-commuting $\hat{W}_{\nu\upsilon}\hat{W}_{\upsilon\nu}$ operators for each quantum number ω_j specified in the wave function of a representation $(\omega, \omega_2 \ldots)$. For an eigenvector υ

$$\begin{aligned}\hat{G}(R_{2l+1})\upsilon &= 1/2(2l-1)^{-1}\sum_{i=1}^{l}(\omega_i+2l-2i+1)\omega_i\upsilon\\ &= g^{ij}(\hat{K}_i\hat{K}_j-\hat{R}_i\hat{R}_j)\\ &= K^2-R^2\end{aligned} \tag{3}$$

in which the vector R is independent of the ω_i. This substitution for the eigenvalues of $\hat{G}$ was made by Racah to simplify derivation of characters of the representations. To derive these characters however, the infinitesimal operators corresponding to K and R must be integrated to finite form. This is possible because an infinite group can be specified either by a single infinite set of infinitesimal operators or by an infinite number of sets of finite operators, the latter being conventionally used to describe representations. Thus the infinitesimal operator $(1 + W_{jj}\delta a^j)$ is is integrated to the matrix $\exp[i W_{jj} a^j]$ in which d^j is a finite angular displacement. In $R_{(2l+1)}$ groups

$$a^j = \theta^{(l+1-j)} \tag{4}$$

to yield the familiar commutation rules [7]. The character of any representation under any operator of $R_{(2l+1)}$ is then the sum over all weights of the representation (different values of ω_i) of the integrated form:

$$\begin{aligned} X(W_1 W_2 \ldots W_l) &= \sum_{\sigma} \exp[i(R)_j \theta^{(l+1-j)}] \\ &= \xi(M) \\ &\quad \frac{\xi(K)}{\xi(R)} \\ &= \frac{\sum_{\sigma} \exp\left[i/2 \sum_{j=1}^{l} (2\omega_j + 2l - 2j + 1)\theta^{(l+1-j)}\right]}{\sum_{\sigma} \exp\left[i/2 \sum_{j=1}^{l} (2l - 2j + 1)\theta^{(l+1-j)}\right]} \end{aligned} \tag{5}$$

Here in the integrated form, the operators (R), are specifically defined as those of the point group which commute with all elements of the group. In the second part of (5) the character is redefined in terms of the Racah vectors of (3) for which there exists a simple expansion. This expression in turn can be reformulated to a ratio of determinants which is more convenient for calculation [4].

The Eq. (5) can be used for subduction between $R_{(2l+1)}$ and R_3 by making a simple substitution. In R_3;

$$\exp\left[i \sum_{j=1}^{l} \hat{W}_{jj} \theta^{(j)}\right] = \exp[i \hat{L} z \theta] \tag{6}$$

that is, the substitution

$$\theta^{(j)} = j\theta$$

may be made. Thus by calculating the character of a representation of $R_{(2l+1)}$ under a group operator W_{jj} with the form of (5) appropriate to R_3, the branching or subduction of that representation is found;

$$\begin{aligned} X(W_1 W_2 \ldots W_l) &= \sum_{L} \frac{\exp[i(L+1/2)\theta] - \exp[-i(L+1/2)\theta]}{\exp[i\theta/2] - \exp[-i\theta/2]} \\ &= \sum_{L} \frac{\sin(L+1/2)\theta}{\sin\theta/2} \end{aligned} \tag{7}$$

As a corrollary, by further specifying in (7) the modulus of any desired quantizing axis, (θ) the characters of representations of finite groups may be subduced from R_3 [8]. These representations are in general reducible and give rise to the familiar reduction tables [9].

Rather than using the Racah vector operator to project simply the character of a representation, using the more complete hypercomplex number projector operators, the eigenfunctions forming the bases to the representations can similarly be obtained from (3) and (4). Each irreducible representation $\Gamma\alpha$ of a point group has a corresponding projection operator [10].

$$\varrho_{ij} = \sum_R \Gamma\alpha(R)^*_{ij} R \tag{8}$$

in which the R are the matrices appropriate to each symmetry operator of the group. Any set of functions which form linear combinations under some operator of the group form a basis of a representation $\Gamma\alpha$. In particular such sets of functions are available in point groups of higher symmetry. Instead of specifying simply the modulus of a quantizing axis of the subgroup however, the behaviour of each operator must be imposed upon the functions of the higher group. This can be formulated as a specialization of (8):

$$\varrho^{\alpha}_{ij} = \sum_{R_G} \Gamma\alpha(R_G)^*_{ij} R_G \delta_{R_G \cdot R_S} \tag{9}$$

in which the projection operators of the generative group G operating on the bases of G are forced by the Kronecker delta function to recognize only those operators appropriate to the subgroup S. Such an operator is clearly independent of the orders of G or S and will be referred to as a Subduction Operator.

An alternative specialization of (8) is possible. If instead of forcing the operators of G to be identical to those of S, the classes of operators C_G of G are forced to match the equivalent classes C_G, of isomorphous group G' then:

$$\varrho^{\alpha}_{ij} = \sum_{R_G} \Gamma\alpha(R_G)^*_{ij} R_G \delta_{C_G C_{G'}} \tag{10}$$

where the bases of G are projected into and onto an isomorphic group G'. Such an operator can be called a Transduction Operator.

3. Subduced Components of Finite Groups

The branching rules (7) and the subduction of components (9) between continuous groups can be used straightforwardly to obtain representations and components in subgroups since all finite axes are colinear with any arbitrary Z axis. The branching of representations from infinite into finite groups again uses (7) since characters are independant of choice of axes. However, the subduction operator (9) may only be used after one axis of the finite subgroup is chosen as the quantizing axis since axes of all moduli are no longer colinear. This is recognized in crystal field theory as a unitary transformation applied to the tensorial sets D_L of R_3 [8, 11]. These transformations mix the components γ_G of the generative group representations Γ_G according to the modulus $|n|$ of the axis chosen for

the (N.S.H.) Hamiltonian H_s of the subgroup. The resulting eigenvectors can therefore be specified as a linear combination formed using Subduction Coefficients:

$$|\Gamma_G H_s \Gamma_s \gamma_s\rangle = \sum_{\gamma_G} (\Gamma_G H_s \gamma_G |n| \,|\, \Gamma_G H_s \Gamma_s \gamma_s) |\Gamma_G H_s \gamma_G |n|\rangle \tag{11}$$

which is a symbolism of the conventional symmetry adaptation procedure [8, 11, 12].

However derivation of Subduction Coefficients by conventional techniques for $l > 3$ can be very tedious and inaccurate if attempted by computer diagonalization techniques. An alternative procedure using vector coupling techniques is available since it is a property of the infinite group that if one degenerate representation is known all the others can be generated. To take advantage of this the relationship between the finite and infinite groups must be defined. This relationship is governed by the transformation properties of the quantizing axis so that the coupling properties of the finite components will be independent of the magnitude of the infinite representation from which they are subduced.

There are available published tabulations of finite group coupling coefficients [8, 13]. None of these however are completely appropriate to the present need because they have invariably been derived without regard to the coupling properties of the components of infinite groups. Our purpose here is to produce a fully real set of phase fixed coupling symbols which mimic the behaviour [4] of Wigner 3-j symbols. In current tabulations [8, 13], imaginary coupling symbols often appear and normalization procedures are arbitrary since no external criteria from higher groups are used. Clearly imaginary coupling symbols cannot arise in a subduction derivation since the subduction procedure using conventional choices of axes does not generate any imaginary coefficients when mapped into a complex basis set and there are no imaginary 3-j symbols for R_3.

4. Derivation and Properties of 3Γ Symbols

Like the components of infinite group representations, the eigenvectors of finite groups couple to give resultant eigenvectors according to definite rules. These rules may either be described by tabulations of the coupling coefficients themselves or by the more symmetric symbols derived by analogy with 3-j symbols. The first of these methods has often been used but leads to very extensive arrays of tables [8] containing many redundancies. The second approach was attempted by Griffith [13] and lead to the definition of a V coefficient. In some ways then V coefficients mimic 3-j symbols but important differences between them remain.

The V coefficients are defined under conditions which require a standardized ordering of eigenvectors. In this way all phase relationships can be fixed. To describe phase changes if components are reordered, an alternating tensor $\varepsilon_{\alpha\beta\gamma}$ is defined. If representations are reordered, the V coefficient must be multiplied by a further phase factor defined by assigning to each octahedral representation a phase defined by its occurance in the symmetric or antisymmetric square.

These two phase definitions produce a self-consistant set of V coefficients but the rules governing their application are very different from those applying to 3-j symbols. It is possible however to redefine the V coefficients to mimic

3-j symbols by the simple device of introducing the l dependence of reduced matrix elements [4] in the infinite group into all the phase conditions. We will distinguish this coupling procedure from that of Griffith by naming coefficients produced under these conditions 3-Γ symbols [14] in analogy with 3-j symbols.

Let $(\Gamma_1^\alpha, \Gamma_2^\beta, \Gamma_3^\gamma \ldots)$ be the components of the irreducible representations of the point group O_h. Further, let $(\psi_{l_1}^a \ldots \psi_{l_1}^n, \psi_{l_2}^a \ldots \psi_{l_2}^n, \psi_{l_3}^a \ldots \psi_{l_3}^n \ldots)$ be the realization of these components in terms of spherical harmonics. Unlike the definition of V coefficients, the 3-Γ symbols will be defined regarding O_h as a group subduced from R_3 on a specific quantizing axis (C_n^z). Then if H_H^x is the Hamiltonian of the system and H_H^h its realization in spherical harmonics;

$$\langle \Gamma_1^\alpha | H_H^x | \Gamma_2^\beta \rangle = C \langle \psi_{l_1}^a | H_H^h | \psi_{l_2}^b \rangle . \tag{12}$$

The constant C is a metric whose phase is dependent on the order of l_1 of the first representation and acts as a scaling factor between H_H^x and H_H^h. Both sides of this equation may be expanded in terms of established definitions. The left side yields Griffith's definition of V coefficients [13] and the right hand side expands to products of subduction coefficients (Sm_i) and the appropriate 3-j symbols;

$$\begin{aligned} &\langle \Gamma_1 \| H_H \| \Gamma_2 \rangle V \begin{pmatrix} \Gamma_1 & \Gamma_2 & H \\ \alpha & \beta & x \end{pmatrix} \\ &= C \sum_{m_i} (Sm_1)^* (Sm_h) (Sm_2) (-1)^{l_1 - m_1} \begin{pmatrix} l_1 & H & l_2 \\ -m_1 & h & m_2 \end{pmatrix} (2l_1 + 1)^{\frac{1}{2}} \langle l_1 \| H \| l_2 \rangle . \end{aligned} \tag{13}$$

It is clear from this expansion that the conventional definition requires the phase factor $(-1)^{l_1 - m_1}$ to be absorbed into the value of the V coefficient. This forces the reduced matrix element of the finite group to be proportional to the V coefficient. In infinite groups the reduced matrix element is always defined as being proportional to the complete coupling coefficient [4] and not just the 3-j symbol. From Eq. (12) the finite and infinite group reduced matrix elements are related by the metric constant C;

$$\langle \Gamma_1 \| H_H \| \Gamma_2 \rangle = C \langle l_1 \| H_H \| l_2 \rangle . \tag{14}$$

Substitution of this condition into (13) will permit direct comparison of the two established coupling schemes. The comparison is further clarified by substituting for the V coefficient, the finite group definition of the coupling coefficient;

$$V \begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma_3 \\ \alpha & \beta & \gamma \end{pmatrix} = \frac{1}{\lambda (\Gamma_2)^{\frac{1}{2}}} \langle \Gamma_1 \alpha | \Gamma_2 \Gamma_3 \beta \gamma \rangle . \tag{15}$$

Then;

$$\begin{aligned} \lambda (\Gamma_1)^{\frac{1}{2}} V \begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma_3 \\ \alpha & \beta & \gamma \end{pmatrix} &= \langle \Gamma_1 \alpha | \Gamma_2 \Gamma_3 \beta \gamma \rangle \\ &= N \sum_{m_i} \langle \psi_{l_1}^a | \psi_{l_2}^h \psi_{l_3}^c \rangle \\ &= N \sum_{m_i} (Sm_1)^* (Sm_2) (Sm_3) (-1)^{l_3 - l_2 - m_1} (2l + 1)^{\frac{1}{2}} \begin{pmatrix} l_1 & l_2 & l_3 \\ -m_1 & m_2 & m_3 \end{pmatrix} \\ &= N F_{l_1 l_2 l_3}^{a\, b\, c} . \end{aligned} \tag{16}$$

The normalization conditions demand that;

$$\sum_{\alpha\beta\gamma} V\begin{pmatrix}\Gamma_1 \Gamma_2 \Gamma_3\\ \alpha\ \beta\ \gamma\end{pmatrix}^2 = \sum_{abc}[\lambda(\Gamma_1)^{-\frac{1}{2}} N F^{a\,b\,c}_{l_1 l_2 l_3}]^2 = 1 \tag{17}$$

and fix the absolute value of the normalizing constant N. The sign of N is fixed by the sign of C in Eq. (14) which arises from the definition [4] of reduced matrix elements of the infinite group;

$$N = |N|(-1)^{l_1} \tag{18}$$

This phase factor (18) was neglected in the original definition of V coefficients. Just as the Wigner Eckart phase factor was absorbed into the V coefficient, this reduced matrix element phase factor was absorbed into the definition of finite group reduced elements. As a result, in some cases the sign of the reduced element depends on the nature of the representation in the bra. This leads either to a non-Hermitian matrix for real reduced elements or to imaginary reduced elements. This in turn implies defining imaginary diagonal V coefficients to obtain real observables.

Inclusion of the sign associated with N in the definition of the coupling symbol Eq. (16) ensures both that the finite group reduced elements must be real and that the coupling symbols will all be real for the complex basis set regardless of the quantization axis. Even though such symbols are formally identical with V coefficients for complex evenfold basis sets we will call entities defined by (16) $3\,\Gamma$ symbols. These will be written simply $\begin{pmatrix}\Gamma_1 \Gamma_2 \Gamma_3\\ \alpha\ \beta\ \gamma\end{pmatrix}$ without the preceding V by analogy with the form of 3-j symbols. The use of $3\,\Gamma$ symbols and their corresponding real reduced elements greatly simplifies the calculation of magnetic properties both under even-fold and odd-fold quantizations.

5. Eigenvector Nomenclature and Selection Rules in $3\,\Gamma$ Symbols

Like 3-j symbols, the selection rules of combination for finite components are reflected in triangular conditions in the $3\,\Gamma$ symbols. Numerical substitutions can be made for both the representation labels Γ and the component labels γ which make these rules very clear in a simple algebraic form.

For components, if the numerical substitution is well designed it can define the vector coupling properties of all components both within the generative group and in all subgroups of a physically significant chain.

The size of the set numbers needed for this nomenclature is governed by the axis modulus $|n|$. The simplest set of numbers fulfilling the requirements of a coupling algebra can thus be directly obtained from the Subduction Operator. In subducing with an axis C^n from R_3, all values

$$0 < m_l < n$$

form such a set. Unlike the behaviour of infinite sets of γ_s however the combinatorial rules for the γ_s must recognize the nature of mapping sums $(\gamma_s + \gamma_{s^1})$ back into the set. The algebra can be further complicated by the size of the largest degeneracy in the subgroup and whether or not this equals the magnitude of the axial modulus.

These difficulties are clearly specific to each group and modulus but need only be solved in practice for the cubic systems O and T because the components of all other cyclic groups of interest can be subduced directly in the appropriate chain. The first criterion of a component nomenclature in the cubic systems is the existence of two representations of order 3, T_1 and T_2. This requires the use of six orthogonal component names but since the two representations are isomorphic the names can be written as generalized product functions:

$$\begin{aligned} &|T_1\, aj\rangle\, |T_1\, bj\rangle\, |T_1\, cj\rangle \\ &|T_2\, ak\rangle\, |T_2\, bk\rangle\, |T_2\, ck\rangle\,. \end{aligned} \tag{19}$$

These component names are necessary and sufficient to characterize all components of the group but their distribution amongst the other representations depends on the axial modulus and must be found using the Subduction Operator. If $|n| \geqq 3$ then a, b, and c are all different in magnitude and/or natural sign but for $|n| < 3$ depending on the axis, some of a, b, and c become identical [3]. The symbols j and k, depending on the quantizing axis act as metrics, each defining a vector space. This reflects the definition of components of T and T_2 in finite groups as eigenvectors but these need not be and indeed are not defined in spaces having the same commutation relationships. Thus, the vector multiplication within the T_1 space (j) is not commutative while that within the T_2 space (k) is. Multiplication of components from the two spaces is permitted subject to the combining rules of the metrics.

The three cases of greatest interest in crystal field theory are the sets of basis functions appropriate to C_4^z, C_3^z, and C_2^z of O_h subduced from R_3. The mapping onto C_4^z has been given in one form [2] but the general theory presented here both justifies it and shows that others are possible [15]. Using (9) under C_4^z the general set and two possible specializations, each having its own rules of combination can be given as:

$$\begin{array}{lll} |A_1\, aj\rangle & |A_1\, 0+\rangle & |A_1\, 0\rangle \\ |A_2\, ak\rangle & |A_2\, 0-\rangle & |A_2\, 2\rangle \\ |E\, aj\rangle & |E\, 0+\rangle & |E\, 0\rangle \\ |E\, ak\rangle & |E\, 0-\rangle & |E\, 2\rangle \\ |T_1\, bj\rangle & |T_1\, 1+\rangle & |T_1\, 1\rangle \\ |T_1\, aj\rangle & |T_1\, 0+\rangle & |T_1\, 0\rangle \\ |T_1\, cj\rangle & |T_1\, -1+\rangle & |T_1\, -1\rangle \\ |T_2\, bk\rangle & |T_2\, 1-\rangle & |T_2\, 1\rangle \\ |T_2\, ak\rangle & |T_2\, 0-\rangle & |T_2\, 2\rangle \\ |T_2\, ck\rangle & |T_2\, -1-\rangle & |T_2\, -1\rangle\,. \end{array} \tag{20}$$

In the first form[3] $j = +$, $k = -$ and a relatively simple centrosymmetric set can be formed. In the third column [15], $|0-\rangle$ is replaced by $|2\rangle$ which eliminates the need for differentiating between j and k but introduces an indeterminacy into the sign appropriate to 2. In fact, for modulus (4)

$$|2\rangle = |-2\rangle \tag{21}$$

and it acts like zero. This indeterminacy must be rectified in the coupling coefficients as an extra phase factor depending on the number of permutations from an agreed standard form. This convention is unnecessary for the first special set and arises because a centrosymmetric set of an even number of component symbols cannot be constructed using a single natural sign. The second "parity" sign used in the first scheme reflects more clearly the fundamentally different commutation behaviour of components and yields phase invariant $3\,\Gamma$ symbols.

A similar set of component symbols can be derived for each of the three quantizations about C_2^z axes of the octahedron. Because the modulus is now |2| and less than the maximum degeneracy the set of six component symbols must be reduced to:

$$\begin{matrix} |\Gamma aj\rangle & |\Gamma ak\rangle \\ |\Gamma bj\rangle & |\Gamma bk\rangle . \end{matrix} \tag{22}$$

The association of component symbols with representations depends on the choice of C_2^z axis reference. Again, various substitutions can be made for a, b, j, and k, one of which is:

$$\begin{matrix} |\Gamma +0+\rangle & |\Gamma +0-\rangle \\ |\Gamma -0+\rangle & |\Gamma -0-\rangle . \end{matrix} \tag{22}$$

This set predicts selection rules essentially from sign conventions at the same time as remaining centrosymmetric in component magnitude. In a system using symbols 0 and 1, the natural sign of 1 is again indeterminate.

The adaption of (19) to trigonal quantization is straightforward. The magnitude of a, b, and c are again all different. A natural centrosymmetric system is created by selection of the lowest value of m in the linear combinations for each component. The metrics $j=+$ and $k=-$ may then be assigned but in a different order to that under C_4^z. During descent on a tetragonal chain the distortion parameters are subduced [2] from the component $|E0+\rangle$. In trigonal chains this is replaced by a component of T_2 [13] implying that metric j must be assigned to this representation. The metric k is assigned to T_1 to preserve the commutation behaviour and these conditions require that both components of E carry metric j. The full assignment is:

$$\begin{aligned} |A_1\, aj\rangle &= |A_1\, 0+\rangle \\ |A_2\, ak\rangle &= |A_2\, 0-\rangle \\ |E\, bj\rangle &= |E\, 1+\rangle \\ |E\, cj\rangle &= |E\, -1+\rangle \\ |T_1\, bk\rangle &= |T_1\, 1-\rangle \\ |T_1\, ak\rangle &= |T_1\, 0-\rangle \\ |T_1\, ck\rangle &= |T_1\, -1-\rangle \\ |T_2\, bj\rangle &= |T_2\, 1+\rangle \\ |T_2\, aj\rangle &= |T_2\, 0+\rangle \\ |T_2\, cj\rangle &= |T_2\, -1+\rangle . \end{aligned} \tag{23}$$

A vector algebra can be simply devised from this nomenclature which unambiguously reproduces the selection rules of the trigonal 3Γ symbols. The set of these symbols is very similar to the V coefficients for tetragonal quantization [13] rearranged slightly to reflect the inverted roles of the E and T_2 representation.

As under C_4^z, the component algebra breaks down into two distinct rules;

6. Component Magnitude Rule

The addition of two component values to yield the third must obey the axial modulus. Thus;

$$\begin{aligned} 1-1&=0 \\ 1+0&=+1 \\ 1+1&=2\rightarrow -1 \\ -1-1&=-2\rightarrow 1 \end{aligned} \tag{24}$$

in which ± 2 is outside the set and must be mapped cyclically back onto 1.

7. Component Sign Rule

The manipulation of signs is identical to that proposed [2] for tetragonal systems. The product of the natural and parity signs of any component is called the total sign. For a 3Γ symbol to exist the product of any two total signs must be the negative of the third total sign.

For neither of the two previously published systems of coefficients [8, 13] can such a simple algebra be designed. For these systems the metrics j and k must act as real and imaginary operators and in the published trigonal V coefficients [13], even this modification requires that some of the postulated V coefficients cannot exist.

The substitution of numerical values for the representation labels is straightforward. In Eq. (16) the 3Γ symbols are related directly to the 3-j symbols from which the finite group functions are subduced. This suggests that the simplest substitution for Γ is the lowest value of l from which Γ can be realized. This scheme makes possible the complete transfer of all infinite group representation selection rules into the finite group. Thus all the triangular conditions on l in 3-j symbols are preserved on Γ in 3Γ symbols. Also retained are the phase relationships governing sign changes induced by the permutation of eigenvectors. Neither of these phase relationships are retained in a similar substitution into V coefficients because of the absorption of phase factors into the value of the corresponding reduced matrix element.

Using 3Γ symbols defined with these component and representation labels, all differences between weak and strong field quantization schemes are removed. This is particularly important in medium field calculations because with either 3Γ symbols in a strong field model or 3-j symbols in a weak field model the same ordering of eigenvalues under all operators must result. The inadvertant inversion of energies between the two models for magnetic operators which can occur using V coefficients is eliminated.

This correspondence between weak and strong field using 3Γ symbols, which essentially arises in Eq. (16) and (18), is achieved because the subducted eigenvectors must display conventional conjugation properties [12a]. The eigenvectors used to define V coefficients are conjugated in the opposite phase to those defined from the application of a subduction operator. This is also true of the more recent tables of coupling coefficients [8] which were again derived from a finite group model. In neither case is there an obvious criterion for the selection of this contrastandard definition.

8. The Normalized Spherical Harmonic Hamiltonian for Trigonal Systems

The Hamiltonian of a point group is the totally symmetric operator eigenstate. Therefore by specifying the axial modulus of the quantizing axis which generates the octahedron, Eq. (7) may be used to select the contributing spherical harmonics from any l manifold. Substituting the C_3^z symmetry operator;

$$X(C_3^z\, Y_l^m) = \frac{\sin(l+\frac{1}{2})\dfrac{2\pi}{3}}{\sin\dfrac{2\pi}{6}}. \tag{25}$$

Dealing with d electrons [4], $l_{\max} = 4$ and reduction of this representation [9, 12] shows that A_1 is contained only in the Y_4^0 and $(Y_4^3 + Y_4^{-3})$ combinations.

In setting up the Subduction Operator a further choice of a second symmetry operator must be made. By convention the defining symmetry operators in the subduction operator will be given in the sequence;

$$\varrho_i = E + C_n^z + C_{n'}^q \tag{26}$$

in which E is the identity, C_n^z the quantizing axis and $C_{n'}^q$ the second necessary operator. There may in some cases be more than one possible choice of $C_{n'}^q$. In general, these choices can lead to different orientations of coordinate axes and by consequence different physically significant chains of subgroups. These choices also often lead to different intermediate symmetry situations particularly if a C_2^z quantizing axis is being used.

Under C_3^z quantization, the x and y axes are indistinguishable and their specific orientation can be chosen for mathematical convenience. However, each choice may produce different sign relationships in the operator eigenstate associated with the Hamiltonian.

The conventional choice of coordinate positions places the y axis coincident with a C_2' axis of the octahedron. The resulting subduction operator is;

$$\varrho = E + C_3^z + C_2'^y + C_2^{(x,y,z)}. \tag{27}$$

This operator fixes the relative signs of Y_4^0 and $(Y_4^3 - Y_4^{-3})$ but does not fix the sign of Y_4^0 itself. If we assume that the nature of the radial parameter is not affected by the selection of a quantizing axis then Y_4^0 must be taken negative. This sign inversion is obtained by subjecting the A_1 operator eigenstate to a unitary trans-

Table 1. Trigonal subduction coefficients to $< = 6$

Γ	γ	l/ml	6	5	4	3	2	1	0	−1	−2	−3	−4	−5	−6
A_1	0^+								1						
		4				$\frac{\sqrt{10}}{\sqrt{27}}$			$\frac{\sqrt{7}}{\sqrt{27}}$			$\frac{-\sqrt{10}}{\sqrt{27}}$			
		6	$\frac{-\sqrt{77}}{9\sqrt{6}}$			$\frac{\sqrt{70}}{9\sqrt{6}}$			$\frac{8}{\sqrt{3}}$			$\frac{+\sqrt{70}}{9\sqrt{6}}$			$\frac{-\sqrt{77}}{9\sqrt{6}}$
A_2	0^-	3				$\frac{\sqrt{2}}{3}$			$\frac{\sqrt{5}}{3}$			$\frac{-\sqrt{2}}{3}$			
		6	$\frac{\sqrt{5}}{3\sqrt{6}}$			$\frac{-\sqrt{22}}{3\sqrt{6}}$						$\frac{-\sqrt{22}}{3\sqrt{6}}$			$\frac{-\sqrt{5}}{3\sqrt{6}}$
E	1^+	2						$\frac{-\sqrt{2}}{\sqrt{3}}$			$\frac{1}{\sqrt{3}}$				
		4			$\frac{\sqrt{7}}{3\sqrt{3}}$			$\frac{-2}{3\sqrt{3}}$			$\frac{-4}{3\sqrt{3}}$				
		5			$\frac{4}{9}$			$\frac{-\sqrt{42}}{9}$			$\frac{\sqrt{3}}{9}$			$\frac{2\sqrt{5}}{9}$	
		6			$\frac{\sqrt{32}}{9}$			$\frac{+\sqrt{12}}{9}$			$\frac{-\sqrt{15}}{9}$			$\frac{-\sqrt{22}}{9}$	
E	$-1+$	2					$\frac{1}{\sqrt{3}}$			$\frac{\sqrt{2}}{\sqrt{3}}$					
		4					$\frac{-4}{3\sqrt{3}}$			$\frac{2}{3\sqrt{3}}$		$\frac{\sqrt{7}}{3\sqrt{3}}$			
		5		$\frac{2\sqrt{5}}{9}$			$\frac{-\sqrt{3}}{9}$			$\frac{-\sqrt{2}}{9}$		$\frac{-4}{9}$			
		6		$\frac{+\sqrt{22}}{9}$			$\frac{-\sqrt{15}}{9}$			$\frac{-\sqrt{12}}{9}$		$\frac{+\sqrt{32}}{9}$			

Table 1 (continued)

Γ	γ	l/ml	6	5	4	3	2	1	0	−1	−2	−3	−4	−5	−6
T_1	1−	1						-1							
		3						$\frac{-1}{\sqrt{6}}$			$\frac{\sqrt{5}}{\sqrt{6}}$				
		4			$\frac{-2}{3\sqrt{2}}$			$\frac{-\sqrt{7}}{3\sqrt{2}}$			$\frac{+\sqrt{7}}{3\sqrt{2}}$				
		5a[a]			$\frac{-13\sqrt{6}}{36\sqrt{3}}$			$\frac{6\sqrt{7}}{36\sqrt{3}}$			$\frac{24\sqrt{2}}{36\sqrt{3}}$			$\frac{7\sqrt{30}}{36\sqrt{3}}$	
		5b[a]			$\frac{\sqrt{35}}{6\sqrt{2}}$			$\frac{\sqrt{30}}{6\sqrt{2}}$						$\frac{\sqrt{7}}{6\sqrt{2}}$	
		6			$\frac{\sqrt{25}}{9\sqrt{2}}$			$\frac{-\sqrt{96}}{9\sqrt{2}}$			$\frac{-\sqrt{30}}{9\sqrt{2}}$			$\frac{\sqrt{11}}{9\sqrt{2}}$	
T_1	0−	1							1						
		3				$-\frac{\sqrt{5}}{\sqrt{18}}$			$\frac{-2}{3}$			$\frac{\sqrt{5}}{\sqrt{18}}$			
		4				$\frac{-1}{\sqrt{2}}$						$\frac{-1}{\sqrt{2}}$			
		5a				$-\frac{\sqrt{5}}{\sqrt{38}}$			$\frac{2\sqrt{7}}{\sqrt{38}}$			$\frac{\sqrt{5}}{\sqrt{38}}$			
		5b				$\frac{\sqrt{14}}{\sqrt{38}}$			$\frac{\sqrt{10}}{\sqrt{38}}$			$\frac{-\sqrt{14}}{\sqrt{38}}$			
		6	$\frac{-\sqrt{22}}{3\sqrt{6}}$			$\frac{-\sqrt{5}}{3\sqrt{6}}$						$\frac{-\sqrt{5}}{3\sqrt{6}}$			$\frac{\sqrt{22}}{3\sqrt{6}}$

Table 1 (*continued*)

Γ	γ	l/ml	6	5	4	3	2	1	0	−1	−2	−3	−4	−5	−6
T_1	−1−	1								1					
		3					$\frac{\sqrt{5}}{\sqrt{6}}$			$\frac{1}{\sqrt{6}}$					
		4					$-\frac{\sqrt{7}}{3\sqrt{2}}$			$\frac{-\sqrt{7}}{3\sqrt{2}}$			$\frac{2}{3\sqrt{2}}$		
		5a		$\frac{-7\sqrt{30}}{36\sqrt{3}}$			$\frac{24\sqrt{2}}{36\sqrt{3}}$			$\frac{-6\sqrt{7}}{36\sqrt{3}}$			$\frac{-13\sqrt{6}}{36\sqrt{3}}$		
		5b		$\frac{-\sqrt{7}}{6\sqrt{2}}$						$\frac{-\sqrt{30}}{6\sqrt{2}}$			$\frac{\sqrt{35}}{6\sqrt{2}}$		
		6		$\frac{\sqrt{11}}{9\sqrt{2}}$			$\frac{\sqrt{30}}{9\sqrt{2}}$			$\frac{-\sqrt{96}}{9\sqrt{2}}$			$\frac{\sqrt{25}}{9\sqrt{2}}$		
T_2	1^+	2						$\frac{1}{\sqrt{3}}$			$\frac{\sqrt{2}}{\sqrt{3}}$				
		3						$\frac{\sqrt{5}}{\sqrt{6}}$			$\frac{1}{\sqrt{6}}$				
		4			$\frac{-2\sqrt{7}}{3\sqrt{6}}$			$\frac{5}{3\sqrt{6}}$			$\frac{1}{3\sqrt{6}}$				
		5			$\frac{-1}{\sqrt{18}}$						$\frac{-2\sqrt{3}}{\sqrt{18}}$			$\frac{\sqrt{5}}{\sqrt{18}}$	
		6a[a]			$\frac{4}{9\sqrt{14}}$			$\frac{7\sqrt{5}}{9\sqrt{14}}$			$\frac{-2\sqrt{30}}{9\sqrt{14}}$			$\frac{8\sqrt{11}}{9\sqrt{14}}$	
		6b[a]			$\frac{-\sqrt{55}}{3\sqrt{14}}$						$\frac{-\sqrt{66}}{9\sqrt{14}}$			$\frac{-\sqrt{5}}{9\sqrt{14}}$	

Table 1 (continued)

Γ	γ	l/ml	6	5	4	3	2	1	0	−1	−2	−3	−4	−5	−6
T_2	0^+	2							1						
		3				$\frac{-1}{\sqrt{2}}$						$\frac{-1}{\sqrt{2}}$			
		4				$\frac{\sqrt{7}}{3\sqrt{6}}$			$\frac{-\sqrt{20}}{3\sqrt{3}}$			$\frac{-\sqrt{7}}{3\sqrt{6}}$			
		5				$\frac{-1}{\sqrt{2}}$						$\frac{-1}{\sqrt{2}}$			
		6a	$\frac{4\sqrt{22}}{9\sqrt{14}\sqrt{3}}$			$\frac{8\sqrt{5}}{9\sqrt{14}\sqrt{3}}$			$\frac{7}{9}$			$\frac{-8\sqrt{5}}{9\sqrt{14}\sqrt{3}}$			$\frac{4\sqrt{22}}{9\sqrt{14}\sqrt{3}}$
		6b	$\frac{-\sqrt{10}}{\sqrt{14}\sqrt{3}}$			$\frac{-\sqrt{11}}{\sqrt{14}\sqrt{3}}$						$\frac{+\sqrt{11}}{\sqrt{14}\sqrt{3}}$			$\frac{\sqrt{10}}{\sqrt{14}\sqrt{3}}$
T_2	$-1+$	2					$\frac{\sqrt{2}}{\sqrt{3}}$			$\frac{-1}{\sqrt{3}}$					
		3					$\frac{1}{\sqrt{6}}$			$\frac{-\sqrt{5}}{\sqrt{6}}$					
		4					$\frac{1}{3\sqrt{6}}$			$\frac{-5}{3\sqrt{6}}$			$\frac{-2\sqrt{7}}{3\sqrt{6}}$		
		5		$\frac{\sqrt{5}}{\sqrt{18}}$			$\frac{2\sqrt{3}}{\sqrt{18}}$						$\frac{1}{\sqrt{18}}$		
		6a		$\frac{-8\sqrt{11}}{9\sqrt{14}}$			$\frac{-2\sqrt{30}}{9\sqrt{14}}$			$\frac{-7\sqrt{6}}{9\sqrt{14}}$			$\frac{4}{9\sqrt{14}}$		
		6b		$\frac{\sqrt{5}}{3\sqrt{14}}$			$\frac{-\sqrt{66}}{3\sqrt{14}}$						$\frac{-55}{3\sqrt{14}}$		

[a] See Appendix.

formation which projects it onto the C_3^{xyz} axis. The resulting trigonally quantized Hamiltonian is;

$$|A_r|_3 = -\frac{\sqrt{7}}{3\sqrt{3}} C_4^0 - \frac{\sqrt{10}}{3\sqrt{3}} C_4^3 + \frac{\sqrt{10}}{3\sqrt{3}} C_4^{-3} \tag{28a}$$

If the roles of the x and y axes are reversed then (27) yields;

$$|A_r|_3' = -\frac{\sqrt{7}}{3\sqrt{3}} C_4^0 + \frac{\sqrt{10}}{3\sqrt{3}} C_4^3 - \frac{\sqrt{10}}{3\sqrt{3}} C_4^{-3}. \tag{28b}$$

An alternative choice of axial positions is possible in which the environments of x and y are equivalent. This is achieved by a $\pi/4$ rotation from the conventional positions and the subduction operator becomes:

$$\varrho = E + C_3^z + C_2^{xy} + C_2^{(xyz)}. \tag{29}$$

The resulting Hamiltonian is;

$$|A_r|_3 = -\frac{\sqrt{7}}{3\sqrt{3}} C_4^0 + \frac{i\sqrt{10}}{3\sqrt{3}} C_4^3 + \frac{i\sqrt{10}}{3\sqrt{3}} C_4^{-3}. \tag{30a}$$

If the second symmetry operator is chosen as either $C_2^{\bar{x}y}$ or $C_2^{x\bar{y}}$ the Hamiltonian is:

$$|A_r|_3 = -\frac{\sqrt{7}}{3\sqrt{3}} C_4^0 - \frac{i\sqrt{10}}{3\sqrt{3}} C_4^3 - \frac{i\sqrt{10}}{3\sqrt{3}} C_4^{-3}. \tag{30b}$$

These four different Hamiltonian operators all yield Hermitian matrices when used on a $|LM_L\rangle$ basis set. However, those matrices from Eq. (28) can contain only real eigenvalues arising from real eigenvectors. On the other hand the operators (30) give Hermitian complex matrices consisting of real diagonal and pure imaginary off-diagonal elements. This matrix also yields fully real eigenvalues but some of the eigenvectors are imaginary.

Each quantization implied in (27) and (29) is associated with a set of symmetry adapted basis functions which reflect the axis position and phase choices. Thus, each of the four Hamiltonian operators (28) and (30) produces a particular set of 3Γ symbols. The sets associated with both operators (28) must themselves be fully real while those accompanying the two complex operators (30) contain some real and some imaginary coefficients. For this reason, the desired real 3Γ symbols to be developed for trigonal quantization are based on the conventional choice of axes and the sign of DQ given in (28a). These symbols are given in Table 1 in terms of magnitudes and relative signs. The signs are related to a standard order of components;

$$\begin{pmatrix} \Gamma_1 \Gamma_2 \Gamma_3 \\ \alpha \ \beta \ \gamma \end{pmatrix} = \begin{pmatrix} \Gamma_1 \Gamma_2 \Gamma_3 \\ 1 \ 0 - 1 \end{pmatrix} \tag{31}$$

by the alternating metric $E_{\alpha\beta\gamma}$ [13] defined only on the components. The metric does not imply reordering of the representations. In cases in which two components of equal magnitude appear, an extra term may be necessary governed by a Kronecker δ $(\alpha\beta)$ function.

Table 2. 3Γ symbols for complex trigonal eigenvectors

	$(\Sigma\Gamma_i)$
$\begin{pmatrix} T_1 T_1 T_1 \\ \alpha\ \beta\ \gamma \end{pmatrix} = \frac{1}{\sqrt{6}} E_{\alpha\beta\gamma}$	3
$\begin{pmatrix} T_1 T_1 T_2 \\ \alpha\ \beta\ \gamma \end{pmatrix} = -\frac{1}{3\sqrt{2}} \lvert E_{\alpha\beta\gamma}\rvert + \frac{\sqrt{2}}{\sqrt{3}} \delta(\alpha,\beta)\,\delta(\beta,\gamma)$	4
$\begin{pmatrix} T_2 T_2 T_2 \\ \alpha\ \beta\ \gamma \end{pmatrix} = \frac{1}{3\sqrt{2}} \lvert E_{\alpha\beta\gamma}\rvert - \frac{\sqrt{2}}{\sqrt{3}} \delta(\alpha,\beta)\,\delta(\beta,\gamma)$	6
$\begin{pmatrix} T_1 T_1 E \\ \alpha\ \beta\ \gamma \end{pmatrix} = \frac{1}{\sqrt{6}} (\lvert E_{\alpha\beta\gamma}\rvert + \delta(\alpha,\beta)\,\delta(\beta,\gamma))\,\delta(\gamma,\pm 1)$	4
$\begin{pmatrix} T_2 T_2 E \\ \alpha\ \beta\ \gamma \end{pmatrix} = \frac{1}{\sqrt{6}} (\lvert E_{\alpha\beta\gamma}\rvert + \delta(\alpha,\beta)\,\delta(\beta,\gamma))\,\delta(\gamma,\pm 1)$	6
$\begin{pmatrix} T_1 T_2 E \\ \alpha\ \beta\ \gamma \end{pmatrix} = -\frac{1}{\sqrt{6}} (E_{\alpha\beta\gamma} + \gamma\,\delta(\alpha,\beta)\,\delta(\beta,\gamma))\,\delta(\gamma,\pm 1)$	5
$\begin{pmatrix} T_2 T_2 T_1 \\ \alpha\ \beta\ \gamma \end{pmatrix} = -\frac{1}{\sqrt{6}} E_{\alpha\beta\gamma}$	5
$\begin{pmatrix} E A_1 E \\ \alpha\ \beta\ \gamma \end{pmatrix} = -\frac{1}{\sqrt{2}} \lvert E_{\alpha\beta\gamma}\rvert\,\delta(\beta,0)$	8
$\begin{pmatrix} E A_2 E \\ \alpha\ \beta\ \gamma \end{pmatrix} = \frac{1}{\sqrt{2}} E_{\alpha\beta\gamma}\,\delta(\beta,0)$	7
$\begin{pmatrix} T_1 A_1 T_1 \\ \alpha\ \beta\ \gamma \end{pmatrix} = \begin{pmatrix} T_2 A_1 T_2 \\ \alpha\ \beta\ \gamma \end{pmatrix} = -\begin{pmatrix} T_1 A_2 T_2 \\ \alpha\ \beta\ \gamma \end{pmatrix} = -\begin{pmatrix} T_2 A_2 T_1 \\ \alpha\ \beta\ \gamma \end{pmatrix} = \frac{1}{\sqrt{3}} \{E_{\alpha\beta\gamma} + \delta(\alpha,\beta)\,\delta(\beta,\gamma)\}\,\delta(\beta,0)$	
$\begin{pmatrix} A_2 A_1 A_2 \\ \alpha\ \beta\ \gamma \end{pmatrix} = -\delta(\alpha,\beta)\,\delta(\beta,\gamma)\,\delta(\gamma,0)$	10

The phase relationships governing the reordering of components in these symbols is given in the last column in Table 1 as a summation of the values of l_i corresponding to the Γ_i.

The subduction coefficients for higher l values may now be developed, as suggested earlier, using Eq. (16). The fully defined 3Γ symbols just discussed now connect any two known subduction coefficients (Sm_1) and (Sm_2) to any unknown (Sm_3) for which the triangular conditions of the 3-j symbol are obeyed. For example if the (Sm_i) for $l=3$ are known the (Sm_3) values for all allowed l values in the direct product;

$$f \times f = s + p + d + f + g + h + i$$

may be determined. The resulting eigenfunctions which retain no ambiguities in conjugation properties are given in Table 2 up to $l=6$.

The subduction of these eigenvectors into trigonal subgroups does not alter the selection rule behaviour defined here. The only effect that descent in symmetry can have on a specific component is to possibly increase the number of selection rules which it must obey [2]. The ramifications of this and the parameters arising from subduced operators are discussed in the following paper.

Appendix. Eigenvalues of Multi-Subduced Representations

Two or more sets of eigenvectors subduced from manifolds of R_3 may bear the same octahedral representation. This occurs in manifolds 5 and 6 which yield two T_1 and two T_2 representations respectively. However the application of Eq. (16) yields only one symmetry adapted eigenvector for each component label γ. Moreover, this new linear combination is not invariant under coupling with the $|A_1 0+|$ operator. It is a linear combination of two orthogonal eigenvectors bearing the same component label in the two interacting representations. The conventional sets of basis functions for $l=5$ or 6 under four fold quantization are those obtained by coupling the subduced eigenvectors and their compliments to the octahedral Hamiltonian. As an example, the coupling of the Hamiltonian with the $|T_1 0+\rangle$ linear combination produced by equation (16) for the $l=5$ manifold yields;

$$\left|\sqrt{\frac{14}{24}}C_4^0+\sqrt{\frac{5}{24}}(C_4^4+C_4^{-4})\right|-\sqrt{\frac{10}{24}}C_5^0+\sqrt{\frac{7}{24}}(C_5^4+C_5^{-4})\rangle=\left|(C_5^4+C_5^{-4})\right\rangle \qquad \text{(A1)}$$

which is a simple multiple of the conventional [12] eigenvector. The other derived $|T_1 0+\rangle$ component is the complement $|C_5^0\rangle$.

These reformulated pairs of eigenvectors, unlike those produced directly by the subduction equation, can be used with the 3Γ symbols to calculate ligand field observables. Of course an infinite variety of methods for splitting the subduced linear combinations into orthogonal pairs could be postulated. However application of the Hamiltonian is consistant with published data on the four fold axis and has therefore been used in this work to derive components of the T_1 ($l=5$) and T_2 ($l=6$) representations.

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