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SYMMETRY ADAPTATION AND WIGNER-RACAH ALGEBRAS IN QUANTUM CHEMISTRY

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Abstract :

The Wigner-Racah algebra of an arbitrary (finite or compact continuous) group is presented in an original way that constitutes a straightforward extension of the corresponding algebra of the rotation group. Illustrative examples are given around the rotation group and the octahedral group. The adaptation of the Wigner-Racah algebra of the double rotation group to one of its subgroups G is discussed in detail. Special emphasis is put on the case where G corresponds to the octahedral group.

The material reported in this work (to be published as an invited paper in a special-subject-issue of Croatica Chemica Acta) has been presented by the author in lectures and seminars on various occasions. The list of references is as complete as possible. However, the author would greatly acknowledge any suggestion concerning further references about Wigner-Racah algebras of interest in molecular physics and quantum chemistry.

I - INTRODUCTION

The determination of matrix elements turns out to be of utmost importance for the application of quantum mechanics to theoretical chemistry. Several methods, among which we must cite the determinantal method of Slater and the tensor method of Racah, exist for determining matrix elements of interest in quantum chemistry. The method of operator equivalents developed by Stevens in crystal-field theory and still used in the formalisms of spin-Hamiltonian and, an another hand, the method of second quantization employed in atomic and molecular spectroscopy may be considered in a certain sense as by-products of the Racah and Slater methods. Each method depends on the form given both to the operators and to the state vectors (or wave functions). The method of Slater lies on the description of the wave functions with the help of determinants and the calculation of matrix elements of one- and two-electron operators can be achieved owing to simple rules, viz., the Slater-Condon rules. The method of Racah is in closer connection with the formulation of quantum mechanics according to Dirac. In this method, the many-electron state vectors are builded from one-electron state vectors with the aid of coupling and recoupling coefficients as well as coefficients of fractional parentage ; further, the physical operators are expanded in terms of (irreducible) tensor operators. The Wigner-Eckart theorem constitutes the basic tool for calculating matrix elements in the framework of Racah's method.

It is well-known that symmetry arguments may lead to important simplifications in the determination of matrix elements. Symmetry considerations enter chemical physics via the introduction of (i) point symmetry groups (e. g., the octahedral group O, the dihedral group D_3, ...) and (ii) classification groups (e. g., the double octahedral group O^*, the special unitary group SU_n, ...).

(i) One or sometimes two point symmetry groups are associated to a given chemical problem. These groups correspond to invariance

groups for the Hamiltonian and for some perturbation to the Hamiltonian of the problem considered. This leads to a chain of invariance groups (e. g., $O \supset D_3$). The use of such groups goes back to the early days of the application of quantum mechanics to chemistry. The interest in invariance groups clearly appears through the Wigner theorem : If an Hamiltonian $\mathcal{H}$ is invariant under a group G, then the eigenfunctions belonging to the same energy eigenvalue of $\mathcal{H}$ span a representation of G. This theorem makes it possible that invariance groups be useful from both a qualitative viewpoint (level splitting, modes of vibration, ...) and a quantitative viewpoint (selection rules, factorization of the secular equation, ...).

(ii) Besides the point symmetry groups, it may be interesting to introduce classification groups. These groups do not correspond to the invariance of Hamiltonians. They arise for the purpose of classifying the state vectors and interactions in view of simplifying the calculation of matrix elements. By way of illustration, we may mention the double (or spinor) groups introduced by Bethe in crystal-field theory for dealing with spin effects in ions with an odd number of electrons ; let us also mention the group SU_5 and the chain $SU_7 \supset G_2$ introduced by Racah for classifying the state vectors and the inter-electronic repulsion Hamiltonian for (atomic) d^N and f^N configurations. For a given problem, the calssification groups are chosen when possible to comprize the point symmetry groups as subgroups so that we generally have a chain of groups involving invariance and classification groups.

The use of group theory is inherent to the method of Racah since this method if often developed in relation with a group or a chain of groups. For example, the method originally introduced by Racah[1] in the theory of complex spectra mainly concerns the rotation group R_3 (or its spinor group SU_2) in the ordinary Cartan-Condon-Shortley basis. In other words, the chain $R_3 \supset C_\infty$ (or $SU_2 \supset U_1$) is the basic group-theoretical ingredient of the original method of Racah. Among the elements of this method which depend of R_3, we have the coupling and recoupling coefficients encountered in the quantum theory of angular momentum. In fact, coupling and recoupling coefficients can

be defined for any group. Along this vein, Wigner[2] independently introduced coupling and recoupling coefficients for simply reducible groups with particular reference to the group SU_2 in a $SU_2 \supset U_1$ basis. The works by Wigner and Racah led to almost the same coupling and recoupling coefficients : the 3-jm and 6-j symbols of Wigner or alternatively the V and W symbols of Racah.

In current terminology, the algebra of the coupling and recoupling coefficients of a group G is referred to as the Wigner-Racah algebra (WRa) of G. The WRa of G constitutes the corner-stone of the (Racah) irreducible tensor method associated to G and permits to render the adaptation to the symmetry G a tool useful from a quantitative viewpoint owing to the Wigner-Eckart theorem for G. In the sixtee's, many works dealt with the WRa of an arbitrary finite or compact group[3] and groups of molecular and solid state interest.[4-7] More specifically, we must mention the work by Tanabe, Sugano, and Kamimura[4] who developed the WRa of the group O in connection with ligand-field theory, the work by Koster and co-workers[5] developed in view of its application to solid state physics, and the work by Griffith[6] also developed in connection with ligand-field theory. In particular, Griffith[6] gave the first detailed treatment for the WRa of molecular symmetry groups with a special attention paid to O and Koster et al.[5] published the first complete set of tables of coupling coefficients for the thirty-two (single and double) crystallographic point groups.

Since the sixtee's, a large amount of works has been devoted to the WRa of groups of chemical interest.[8-34] More particularly, the WRa of a subgroup G of R_3 has been fully investigated by considering G either as an isolated entity or as a group linked to R_3. In the latter direction, following a work by Racah and some of his students (cf., Ref. 8) on the construction of the energy matrix of d^N ions in cubical, tetragonal, or trigonal crystalline fields, the author studied the WRa of SU_2 in a nonstandard $SU_2 \supset G$ basis.[13]

This paper deals with many aspects of the WRa of groups of

importance in chemistry. The grounds of the WRa of an arbitrary compact group G are presented in Sec. II in a way that fully parallels the classic exposure of the WRa of the group R_3 in a $R_3 \supset C_\infty$ basis. We consider in Sec. III some illustrative examples and in Sec. IV the special case of the WRa of SU_2 in a $SU_2 \supset G$ basis, where G stands for the double group of a point rotation group. As a by-product, we demonstrate in Sec. V how to obtain the coupling coefficients of G with emphasis on the particular case of the group O.

II - WIGNER-RACAH ALGEBRA

1 - Preliminaries

We begin with an arbitrary finite or compact continuous group G having the irreducible representations classes (IRC's) a, b, c,... . The identity IRC, customarily noted A_1 or Γ_1 in theoretical chemistry, is denoted here by 0. To each IRC a, we associate a unitary matrix representation $\mathcal{D}^a$. Let [a] be the dimension of $\mathcal{D}^a$. The α-α' matrix element of the representative $\mathcal{D}^a(R)$ for the element R in G is written $\mathcal{D}^a(R)_{\alpha\alpha'}$. (For a = 0, we use $\alpha = \alpha' = 0$.) The sum $\chi^a(R) = \sum_\alpha \mathcal{D}^a(R)_{\alpha\alpha}$ stands for the character of R in $\mathcal{D}^a$. The $\mathcal{D}^a(R)_{\alpha\alpha'}$ and $\chi^a(R)$ satisfy orthogonality relations (cf., the so-called great orthogonality theorem) that are very familiar to the chemist. Finally, note that $\int_G dR \ldots$ identifies to $\sum_{R \in G} \ldots$ and that $|G| = \int_G dR$ corresponds to the order of G in the case where G is a finite group.

2 - Clebsch-Gordan coefficients

The direct product $a \otimes b$ of two IRC's a and b of G can be in general decomposed into a direct sum of IRC's of G. This leads to the Clebsch-Gordan series

$$a \otimes b = \bigoplus_c \sigma(c|a \otimes b)\, c \qquad (1)$$

where $\sigma(c|a\otimes b)$ denotes the number of times the IRC c occurs in $a\otimes b$. The determination of the integers $\sigma(c|a\otimes b)$ may be achieved through the character formula

$$\sigma(c|a\otimes b) = |G|^{-1}\int_G dR\ \chi^c(R)^*\chi^a(R)\ \chi^b(R) \tag{2}$$

In terms of matrix representations, Eq. (1) reads

$$\mathfrak{D}^a\otimes\mathfrak{D}^b \sim \bigoplus_c \sigma(c|a\otimes b)\mathfrak{D}^c \tag{3}$$

Therefore, there exists a unitary matrix U^{ab} such that

$$(U^{ab})^\dagger\,\mathfrak{D}^a(R)\otimes\mathfrak{D}^b(R)\,U^{ab} = \bigoplus_c \sigma(c|a\otimes b)\mathfrak{D}^c(R) \tag{4}$$

$$\mathfrak{D}^a(R)\otimes\mathfrak{D}^b(R) = U^{ab}\bigoplus_c \sigma(c|a\otimes b)\mathfrak{D}^c(R)\,(U^{ab})^\dagger \tag{5}$$

for any R in G. It is a simple exercice in linear algebra to transcribe Eqs. (4) and (5) in matrix elements. We thus have

$$\sum_{\alpha\beta\alpha'\beta'} (ab\alpha\beta|\rho c\,\gamma)^*\,\mathfrak{D}^a(R)_{\alpha\alpha'}\,\mathfrak{D}^b(R)_{\beta\beta'}\,(ab\alpha'\beta'|\rho' c'\gamma') = \Delta(c|a\otimes b)\,\delta(\rho'\rho)\,\delta(c'c)\,\mathfrak{D}^c(R)_{\gamma\gamma'} \tag{6}$$

$$\mathfrak{D}^a(R)_{\alpha\alpha'}\,\mathfrak{D}^b(R)_{\beta\beta'} = \sum_{\rho c\,\gamma\gamma'} (a\,b\alpha\beta|\rho\,c\,\gamma)\,\mathfrak{D}^c(R)_{\gamma\gamma'}\,(a\,b\alpha'\beta'|\rho\,c\,\gamma')^* \tag{7}$$

for any R in G. In Eqs. (6) and (7), $(a\,b\alpha\beta|\rho\,c\,\gamma)$ stands for an element of the matrix U^{ab}:

$$(a\,b\alpha\beta|\rho\,c\,\gamma) = (U^{ab})_{\alpha\beta,\rho\,c\,\gamma} \tag{8}$$

Each row index of U^{ab} consists of two labels (α and β) according to the rules of the direct product of two matrices. This is indeed the same thing for each column index of U^{ab} : two labels (c and γ) are required. However, when c appears several times in $a \otimes b$, a third label (the multiplicity label ρ) is necessary besides c and γ. Hence, the summation over ρ in Eq. (7) ranges from 1 to $\sigma(c|a \otimes b)$. Finally, in Eq. (6), δ denotes the usual Kronecker delta while $\Delta(c|a \otimes b) = 0$ or 1 according to whether as c is contained or not in $a \otimes b$.

The matrix elements $(a\, b\, \alpha\, \beta | \rho\, c\, \gamma)$ are termed Clebsch-Gordan coefficients (CGc's) or vector coupling coefficients. Their present introduction clearly emphasizes that the CGc's of a group G are nothing but the elements of the unitary matrix which reduces the direct product of two irreducible matrix representations of G. As a consequence, the CGc's satisfy two orthonormality relations associated to the unitary property of U^{ab}:

$$\sum_{\alpha\beta} (a\, b\, \alpha\, \beta | \rho\, c\, \gamma)^* (a\, b\, \alpha\, \beta | \rho'\, c'\, \gamma') = \Delta(c|a \otimes b)\, \delta(\rho'\rho)\, \delta(c'c)\, \delta(\gamma'\gamma) \qquad (9)$$

$$\sum_{\rho\, c\, \gamma} (a\, b\, \alpha\, \beta | \rho\, c\, \gamma)\, (a\, b\, \alpha'\, \beta' | \rho\, c\, \gamma)^* = \delta(\alpha'\alpha)\, \delta(\beta'\beta) \qquad (10)$$

Note that Eqs.(9) and (10) are conveniently recovered by specializing R to the unit element E of G in Eqs. (6) and (7), respectively.

Equations (6) and (7) show that the CGc's are basis-dependent coefficients. In this regard, it is important to realize that Eqs. (6) and (7) are not sufficient to define unambigously the CGc's of the group G once its irreducible representation matrices are known. As a matter of fact, the relation

$$(a\, b\, \alpha\, \beta | r\, c\, \gamma) = \sum_{\rho} (a\, b\, \alpha\, \beta | \rho\, c\, \gamma)\; M(a\, b, c)_{\rho r} \qquad (11)$$

where $M(a\, b, c)$ is an arbitrary unitary matrix, defines a new set of CGc's

since Eqs. (6) and (7) are satisfied by making replacements of the type $\rho \to r$. The CGc's associated to a definite choice for the irreducible representation matrices of G are thus defined up to a unitary transformation, a fact that may be exploited to generate special properties of the CGc's.

Various relations involving elements of irreducible representation matrices and CGc's can be derived from Eqs. (6) and (7) by using the unitary property both for the representation matrices and the Clebsch-Gordan matrices. For instance, from Eq. (6) we obtain

$$\sum_{\alpha'\beta'} \mathcal{D}^a(R)_{\alpha\alpha'} \mathcal{D}^b(R)_{\beta\beta'} (a\, b\alpha'\beta' | \rho\, c\, \gamma') = \sum_{\gamma} \mathcal{D}^c(R)_{\gamma\gamma'} (a\, b\alpha\beta | \rho c \gamma) \qquad (12)$$

$$(a\, b\alpha'\beta' | \rho c \gamma') = \sum_{\alpha\beta\gamma} (a\, b\alpha\beta | \rho c \gamma) \mathcal{D}^a(R)^*_{\alpha\alpha'} \mathcal{D}^b(R)^*_{\beta\beta'} \mathcal{D}^c(R)_{\gamma\gamma'} \qquad (13)$$

for any R in G. In the situation where the elements of the irreducible representation matrices of G are known, Eq. (12) or (13) provides us with a system of linear equations useful for the calculation of the CGc's of G.

The combination of Eq. (7) with the great orthogonality theorem for G yields the integral relation

$$|G|^{-1} \int_G dR\, \mathcal{D}^a(R)_{\alpha\alpha'} \mathcal{D}^b(R)_{\beta\beta'} \mathcal{D}^c(R)^*_{\gamma\gamma'} = [c]^{-1} \sum_{\rho} (a\, b\alpha\beta | \rho\, c\, \gamma) (a\, b\alpha'\beta' | \rho\, c\, \gamma')^* \qquad (14)$$

which also is useful for the calculation of the CGc's of G in terms of the elements of the irreducible representation matrices of G. Note that when $a \otimes b$ is multiplicity-free (i.e., when there is no summation on ρ in Eq. (14)), Eq. (14) allows us to determine the $(a\, b\alpha\beta | c\, \gamma)$ for all α, β, and γ up to an arbitrary phase factor $h(a\, b, c)$; more precisely, we then have

$$(a\,b\,\alpha\,\beta\,|\,c\,\gamma) = e^{i\,h(a\,b,c)} \int_G dR\, \mathcal{D}^a(R)_{\alpha\alpha'}\, \mathcal{D}^b(R)_{\beta\beta'}\, \mathcal{D}^c(R)_{\gamma\gamma'}{}^*$$

$$\left\{ (|G|/|c|) \int_G dR\, \mathcal{D}^a(R)_{\alpha'\alpha'}\, \mathcal{D}^b(R)_{\beta'\beta'}\, \mathcal{D}^c(R)_{\gamma'\gamma'}{}^* \right\}^{-1/2} \qquad (15)$$

It appears from Eqs. (12)-(15) that c does not generally play the same role as a and b in $(a\,b\,\alpha\,\beta\,|\,\rho\,c\,\gamma)$. Therefore, $(a\,b\,\alpha\,\beta\,|\,\rho\,c\,\gamma)$ does not generally exhibit simple symmetry properties under permutation of a, b, and c. It is to be showed in the following how the CGc's may be symmetrized thanks to a 2-aα symbol.

3 - The 2 - aα symbol

Let us define the 2-aα symbol through

$$\begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix} = [a]^{1/2}\, (b\,a\,\beta\,\alpha\,|\,0\,0) \qquad (16)$$

The 2-aα symbol makes it possible to pass from a given irreducible matrix representation to its complex conjugate. This is reflected by the two relations

$$\sum_{\alpha\alpha'} \begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix}^* \mathcal{D}^a(R)_{\alpha\alpha'} \begin{pmatrix} a & b' \\ \alpha' & \beta' \end{pmatrix} = \Delta\,(0|\,a \otimes b)\, \delta\,(b'b)\, \mathcal{D}^b(R)_{\beta\beta'}{}^* \qquad (17)$$

$$\sum_{\beta\beta'} \begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix} \mathcal{D}^b(R)_{\beta\beta'}{}^* \begin{pmatrix} a' & b \\ \alpha' & \beta' \end{pmatrix}^* = \Delta\,(0|\,a \otimes b)\, \delta\,(a'\,a)\, \mathcal{D}^a(R)_{\alpha\alpha'} \qquad (18)$$

that hold for any R in G. The proof of Eqs. (17) and (18) is delicate ; it starts with the introduction of Eq. (16) into the left-hand sides of Eqs. (17) and (18) and requires the successive use of Eqs. (13), (7), (9), and (13), of the great orthogonality theorem, and of Eq. (9). By taking R = E in Eqs. (17) and (18), we get the following useful relations

$$\sum_{\alpha} \begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix}^{*} \begin{pmatrix} a & b' \\ \alpha & \beta' \end{pmatrix} = \Delta\,(0|a \otimes b)\,\delta\,(b'b)\,\delta\,(\beta'\beta) \tag{19}$$

$$\sum_{\beta} \begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix} \begin{pmatrix} a' & b \\ \alpha' & \beta \end{pmatrix}^{*} = \Delta\,(0|a \otimes b)\,\delta\,(a'a)\,\delta\,(\alpha'\alpha) \tag{20}$$

The 2-aα symbol turns out to be of relevance for handling phase problems. In this respect, both Eqs. (17) and (18) lead to

$$\delta\,(a'a) \sum_{\alpha\alpha'} \begin{pmatrix} a & a' \\ \alpha & \alpha' \end{pmatrix}^{*} \begin{pmatrix} a' & a \\ \alpha' & \alpha \end{pmatrix} = \Delta\,(0|a \otimes a')\,[a]\,c_a \tag{21}$$

where the Frobenius-Schur coefficient

$$c_a = |G|^{-1} \int_G dR\ \chi^a\,(R^2) \tag{22}$$

is 1, -1, or 0 according to whether as $\mathfrak{D}^a$ is orthogonal, symplectic, or complex. The Frobenius-Schur theorem concerning the conjugating matrix to pass from $\mathfrak{D}^a$ to $(\mathfrak{D}^a)^*$ may then be expressed by

$$c_a \begin{pmatrix} a' & a \\ \alpha' & \alpha \end{pmatrix} = \delta\,(a'a) \begin{pmatrix} a & a' \\ \alpha & \alpha' \end{pmatrix} \tag{23}$$

4 - <u>The (3-aα)$_\rho$ symbol</u>

We now define the (3-aα)$_\rho$ symbol via

$$\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_\rho = \sum_{\rho'c'\gamma'} [c']^{-1/2}\, M(ba,c')_{\rho'\rho} \begin{pmatrix} c & c' \\ \gamma & \gamma' \end{pmatrix} (ba\,\beta\alpha\,|\rho'c'\gamma') \tag{24}$$

where M(ba,c') is an arbitrary unitary matrix. Conversely, each CGc can be developed in terms of (3-aα)$_\rho$ symbols since the inversion of Eq. (24) gives

$$(a\,b\alpha\beta|\rho\,c\,\gamma) = [c]^{1/2} \sum_{\rho'c'\gamma'} M(ab,c)_{\rho\rho'}{}^{*} \begin{pmatrix} c' & c \\ \gamma' & \gamma \end{pmatrix}^{*} \begin{pmatrix} b & a & c' \\ \beta & \alpha & \gamma' \end{pmatrix}_{\rho'} \qquad (25)$$

All the relations involving CGc's may be transcribed in function of $(3\text{-}a\alpha)_\rho$ symbols. For example, the introduction of Eq. (25) into Eqs. (6) and (7) yields after nontrivial calculations

$$\sum_{\alpha\beta\alpha'\beta'} \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_{\rho}^{*} \mathcal{D}^{a}(R)_{\alpha\alpha'}\, \mathcal{D}^{b}(R)_{\beta\beta'} \begin{pmatrix} a & b & c' \\ \alpha' & \beta' & \gamma' \end{pmatrix} \qquad (26)$$

$$= \Delta(0|a \otimes b \otimes c)\, \delta(\rho'\rho)\, \delta(c'c)\, [c]^{-1}\, \mathcal{D}^{c}(R)_{\gamma\gamma'}{}^{*}$$

$$\mathcal{D}^{a}(R)_{\eta\alpha'}\, \mathcal{D}^{b}(R)_{\beta\beta'} = \sum_{\rho\, c\, \gamma\gamma'} [c] \qquad (27)$$

$$\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_{\rho} \mathcal{D}^{c}(R)_{\gamma\gamma'}{}^{*} \begin{pmatrix} a & b & c \\ \alpha' & \beta' & \gamma' \end{pmatrix}_{\rho}^{*}$$

for any R in G. The orthogonality relations

$$\sum_{\alpha\beta} \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_{\rho}^{*} \begin{pmatrix} a & b & c' \\ \alpha & \beta & \gamma' \end{pmatrix}_{\rho'} = \Delta(0|a \otimes b \otimes c)\, \delta(\rho'\rho)\, \delta(c'c)\, \delta(\gamma'\gamma)[c]^{-1} \qquad (28)$$

$$\sum_{\rho c \gamma} [c] \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_{\rho} \begin{pmatrix} a & b & c \\ \alpha' & \beta' & \gamma \end{pmatrix}_{\rho}^{*} = \delta(\alpha'\alpha)\, \delta(\beta'\beta) \qquad (29)$$

follow by putting R = E in Eqs. (26) and (27).

Relation (26) and its dual relation (27) show that $\mathcal{D}^{a}$, $\mathcal{D}^{b}$, and $\mathcal{D}^{c}$ present the same variance. Thus, the behaviour of the symbol $\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_{\rho}$ under permutation of a, b, and c should be easier to describe than the one of the CGc $(ab\alpha\beta|\rho c\gamma)$. This is reflected by the integral relation (to be compared

to Eq. (14))

$$|G|^{-1} \int_G dR \; \mathfrak{D}^a(R)_{\alpha\alpha'} \; \mathfrak{D}^b(R)_{\beta\beta'} \; \mathfrak{D}^c(R)_{\gamma\gamma'} = \sum_\rho \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_\rho \begin{pmatrix} a & b & c \\ \alpha' & \beta' & \gamma' \end{pmatrix}_\rho^* \qquad (30)$$

which may be proved directly by combining Eq. (27) with the great orthogonality theorem for the group G. When the triple direct product $a \otimes b \otimes c$ contains the IRC 0 of G only once (i.e., when there is no summation on ρ in Eq. (30)), Eq. (30) shows that $|\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}|^2$ is invariant under permutation of its columns. In this case, we may take advantage of the arbitrariness of the matrix M in Eq. (11) or (24) to produce convenient symmetry properties of the symbol $\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}$ under permutation of its columns. As an illustration, let us mention the following result (*cf.*, Ref. 2) : for G simply reducible, it is possible to arrange that the numerical value of $\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}$ be multiplied by the phase factor $(-1)^{a+b+c}$, with $(-1)^{2x} = c_x$, under an odd permutation of its columns ; consequently, the numerical value of $\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}$ remains unchanged (since $c_a \, c_b \, c_c = 1$) under an even permutation of its columns.

5 - Recoupling coefficients

We now define two new coefficients

$$(a(bc)\,\rho_{bc}\,c_{bc}\,\rho' d' \delta' | (ab)\,\rho_{ab}\,c_{ab}\,c\,\rho\, d\,\delta) = \sum_{\alpha\beta\gamma\gamma_{ab}\gamma_{bc}} (bc\beta\gamma|\rho_{bc}\,c_{bc}\,\gamma_{bc})^* \, (a\,c_{bc}\,\alpha\,\gamma_{bc}|\rho' d' \delta')^* \, (ab\alpha\beta|\rho_{ab}\,c_{ab}\,\gamma_{ab}) \, (c_{ab}\,c\,\gamma_{ab}\,\gamma|\rho\, d\,\delta) \qquad (31)$$

$$((ac)\,\rho_{ac}\,c_{ac}\,(bd)\rho_{bd}\,c_{bd}\,\rho' e' \varepsilon' | (ab)\,\rho_{ab}\,c_{ab}\,(cd)\,\rho_{cd}\,c_{cd}\,\rho\, e\,\varepsilon) = \sum_{\alpha\beta\gamma\delta\gamma_{ab}\gamma_{cd}\gamma_{ac}\gamma_{bd}} \qquad (32)$$

$$(ac\,\alpha\,\gamma\,|\rho_{ac}\,c_{ac}\,\gamma_{ac})^{*}\,(bd\,\beta\,\delta\,|\rho_{bd}\,c_{bd}\,\gamma_{bd})^{*}\,(c_{ac}\,c_{bd}\,\gamma_{ac}\,\gamma_{bd}\,|\rho'e'\,\varepsilon')^{*}$$

$$(ab\,\alpha\,\beta\,|\rho_{ab}\,c_{ab}\,\gamma_{ab})\,(cd\,\gamma\,\delta\,|\rho_{cd}\,c_{cd}\,\gamma_{cd})\,(c_{ab}\,c_{cd}\,\gamma_{ab}\,\gamma_{cd}\,|\rho\,e\,\varepsilon)$$

The introduction in these definitions of Eq. (13) and the use of the great orthogonality theorem for G leads to the properties

$$(a(bc)\rho_{bc}\,c_{bc}\,\rho'\,d'\,\delta'\,|(ab)\,\rho_{ab}\,c_{ab}\,c\,\rho\,d\,\delta) = \delta\,(d'd)\,\delta\,(\delta'\,\delta)\,[d]^{-1}$$

$$\sum_{\delta}\,(a\,(bc)\,\rho_{bc}\,c_{bc}\,\rho'd\,\delta\,|(ab)\;\;\rho_{ab}\,c_{ab}\,c\,\rho\,d\,\delta) \tag{33}$$

$$((ac)\,\rho_{ac}\,c_{ac}\,(bd)\,\rho_{bd}\;\;c_{bd}\,\rho'\;e'\;\varepsilon'\,|(ab)\,\rho_{ab}\,c_{ab}\,(cd)\,\rho_{cd}\,c_{cd}\,\rho\;e\;\varepsilon)$$

$$= \delta\,(e'e)\,\delta\,(\varepsilon'\varepsilon)\,[e]^{-1}\sum_{\varepsilon} \tag{34}$$

$$((ac)\,\rho_{ac}\,c_{ac}\,(bd)\,\rho_{bd}\,c_{bd}\,\rho'\;e\;\varepsilon\,|(ab)\,\rho_{ab}\,c_{ab}(cd)\,\rho_{cd}\,c_{cd}\,\rho\;e\;\varepsilon)$$

so that the recoupling coefficients defined by Eqs. (31) and (32) are basis-independent (i.e., they do not depend on the labels of type α) in contradistinction with the coupling coefficients $(a\,b\,\alpha\,\beta|\rho\,c\,\gamma)$. Note that, in a way paralleling the passage from the coupling coefficients to the $(3\text{-}a\alpha)_{\rho}$ symbol, it is possible to define $(6\text{-}a)_{4\rho}$ and $(9\text{-}a)_{6\rho}$ symbols from the recoupling coefficients defined by Eqs. (31)-(34), respectively. The defining expressions of the $(6\text{-}a)_{4\rho}$ and $(9\text{-}a)_{6\rho}$ symbols are very complicated and not especially instructive in the case of an arbitrary compact group G. Hence, they shall be omitted here as well as the defining expressions for higher $(3(n-1)\text{-}a)_{2(n-1)\rho}$ symbols corresponding to the recoupling of $n > 4$ IRC's.

6-Irreducible tensorial sets

Let $\{\,|\tau\,a\,\alpha) : \alpha$ ranging $\{$ be a basis for the irreducible matrix

representation $\mathfrak{D}^a$ of G. The vectors $|\tau a \alpha)$ are defined on a unitary or pre-Hilbert space $\mathfrak{E}$ (indeed, a Hilbert space in the quantum-mechanical applications) and there exists an application $R \to P_R$ such that

$$P_R |\tau a \alpha) = \sum_{\alpha'=1}^{[a]} |\tau a \alpha') \mathfrak{D}^a(R)_{\alpha'\alpha} \tag{35}$$

for any R in G. The set $\{|\tau a \alpha) : \alpha \text{ ranging}\}$ is referred to as an irreducible tensorial set (ITS) of vectors associated to $\mathfrak{D}^a$. The label τ may serve to distinguish the various ITS' of vectors associated to the same irreducible matrix representation $\mathfrak{D}^a$. (In practical applications, this label consists of various quantum numbers arising from atomic or molecular configurations.) In this connection, note the following standardization : it is always possible to arrange that $\{|\tau a \alpha) : \alpha \text{ ranging}\}$ and $\{|\tau' a \alpha) : \alpha \text{ ranging}\}$ span the same representation $\mathfrak{D}^a$ rather than two equivalent representations.

From the two ITS' $\{|\tau_a a \alpha) : \alpha \text{ ranging}\}$ and $\{|\tau_b b\beta : \beta \text{ ranging}\}$, we can construct another ITS of vectors. Let us define

$$|\tau_a \tau_b a\, b\, \rho\, c\, \gamma) = \sum_{\alpha\,\beta} |\tau_a a \alpha)|\tau_b b\beta)\, (a\, b\, \alpha\beta |\rho c \gamma) \tag{36}$$

Then, as a simple corollary of Eq. (7), we may prove that $\{|\tau_a \tau_b a\, b \rho\, c \gamma) : \gamma \text{ ranging}\}$ is an ITS associated to $\mathfrak{D}^c$.

In a similar way, let us consider a set $\{T^a_\alpha : \alpha \text{ ranging}\}$ of (linear) operators defined on $\mathfrak{E}$ and such that

$$P_R\, T^a_\alpha\, P_R^{-1} = \sum_{\alpha'=1}^{[a]} T^a_{\alpha'}\, \mathfrak{D}^a(R)_{\alpha'\alpha} \tag{37}$$

for any R in G. This set is referred to as an ITS of operators associated to $\mathfrak{D}^a$. We also say that this set defines an irreducible tensor operator $\mathbf{T}^a$ associated to $\mathfrak{D}^a$. Note the implicit standardization : the sets $\{T^a_\alpha : \alpha \text{ ranging}\}$ and $\{U^a_\alpha : \alpha \text{ ranging}\}$ span the same representation $\mathfrak{D}^a$ rather than two equivalent representations.

In full analogy with Eq. (36), we define

$$\{T^a \otimes U^b\}^{\rho c}_{\gamma} = \sum_{\alpha\beta} T^a_\alpha U^b_\beta (a b \alpha \beta | \rho c \gamma) \tag{38}$$

from the two ITS' $\{T^a_\alpha : \alpha \text{ ranging}\}$ and $\{U^a_\beta : \beta \text{ ranging}\}$. As a net result, the set

$\{\{T^a \otimes U^b\}^{\rho c}_{\gamma} : \gamma \text{ ranging}\}$ is an ITS of operators associated to $\mathfrak{D}^c$. We say that $\{\mathbf{T}^a \otimes \mathbf{U}^b\}$ is the direct product of the irreducible tensor operators $\mathbf{T}^a$ and $\mathbf{U}^b$. Observe that this direct product defines a tensor operator which is reducible in general. Equation (38) gives the various irreducible components of $\{\mathbf{T}^a \otimes \mathbf{U}^b\}$.

7 - Wigner-Eckart theorem

The connection between most of the quantities introduced up to now appears in the calculation of the matrix element $(\tau' a' \alpha' | T^b_\beta | \tau a \alpha)$, the scalar product on $\mathcal{E}$ of the vector $T^b_\beta | \tau a \alpha)$ by the vector $| \tau' a' \alpha')$. By developing the identity (cf., $P_R^\dagger P_R$ is the unit operator)

$$(\tau' a' \alpha' | T^b_\beta | \tau a \alpha) = (\tau' a' \alpha' | P_R^\dagger P_R T^b_\beta P_R^{-1} P_R | \tau a \alpha) \tag{39}$$

we get after some manipulations the basic result

$$(\tau' a' \alpha' | T^b_\beta | \tau a \alpha) = \sum_\rho (\tau' a' || T^b || \tau a)_\rho \sum_{\alpha'' \alpha''} \begin{pmatrix} a'' & a' \\ \alpha'' & \alpha' \end{pmatrix} \begin{pmatrix} b & a & a'' \\ \beta & \alpha & \alpha'' \end{pmatrix}^*_\rho \tag{40}$$

Alternatively, Eq. (40) can be cast in the form

$$(\tau' a' \alpha' | T^b_\beta | \tau a \alpha) = [a']^{-1/2} \sum_\rho \sum_{\rho'} M(ab, a')^*_{\rho', \rho} \quad (41)$$

$$(\tau' a' || T^b || \tau a)_\rho \, (a b \alpha \beta | \rho' a' \alpha')^*$$

The so-called reduced matrix elements $(\tau' a' || T^b || \tau a)_\rho$ in Eqs. (40) and (41) do not depend on the labels α', β, and α and therefore, like the recoupling coefficients, are basis-independent. We then understand the interest of the recoupling coefficients in applications : the reduced matrix elements for a composed system may be developed as functions of reduced matrix elements for elementary systems and recoupling coefficients. In this direction, it can be verified that the matrix element

$(\tau_a' \tau_b' a' b' \rho' c' \gamma' | \{ T^d \circledast U^e \}^{\sigma f}_{\psi} | \tau_a \tau_b a b \rho c \gamma)$ can be expressed in terms of the recoupling coefficients defined by Eqs. (32) and (34).

Equations (40) and (41) generalize the Wigner-Eckart theorem originally derived by Eckart for vector operators of the rotation group, by Wigner for tensor operators of the rotation group and of simply reducible groups, and by Racah for tensor operators of the rotation group.

It is important to realize that no phase factors of the type $(-1)^a$, $(-1)^{a-\alpha}$, and $(-1)^{a+b+c}$ appear in Eqs. (40) and (41). Indeed, the present exposure of the WRa of an arbitrary compact group is entirely free of such phase factors, in contrast with other works. As a matter of fact, in many works the passage from the Clebsch-Gordan or unsymmetrical form to the $(3\text{-}a\alpha)_\rho$ or symmetrical form of the coupling coefficients involves unpleasant questions of phase. This is not the case in Eqs. (24) and (25). Such a fact does not mean that Eqs. (24) and (25) as well as the other general relations of Sec. II are free of arbitrary phase factors. In fact, all the phase factors are implicitly contained in the matrices M, the 2-$a\alpha$ symbols, and the (basis-

independent) Frobenius-Schur coefficient.

III - ILLUSTRATIVE EXAMPLES

1 - The rotation group

We shall indeed deal with the universal covering or, in the terminology of crystal-field theory, the double group SU_2 of the rotation group R_3. In this case, $a \equiv j$ is either an integer (for vector representations) or a half-an-odd integer (for spinor representations), $\alpha \equiv m$ ranges from -j to j by unit step, and $\mathcal{D}^a(R)_{\alpha\alpha'}$ identifies to the element $\mathcal{D}^j(R)_{mm'}$ of the well-known Wigner rotation matrix of dimension $[j] \equiv 2j + 1$. The matrix representation $\mathcal{D}^j$ corresponds to the standard basis $\{|jm) : m = -j(1)j\}$ where $|jm)$ denotes an eigenvector of the angular momentum operators J^2 and J_z. (For j integer, the label ℓ often replaces j.) The labels of type m clearly refer to IRC's of the rotation group $C_\infty \sim R_2$ or its double group U_1. Therefore, the basis $\{|jm) : m = -j(1)j\}$ is called an $R_3 \supset R_2$ or $SU_2 \supset U_1$ basis. Further, the multiplicity label ρ is not necessary since SU_2 is multiplicity-free. Consequently, the (real) CGc's of SU_2 in a $SU_2 \supset U_1$ basis are written $(j_1 j_2 m_1 m_2 \,|jm)$.

In view of the ambivalent nature of SU_2, the 2-aα symbol reduces to a 1-jm symbol. More specifically, Eq. (16) specializes to

$$\begin{pmatrix} j & j' \\ m & m' \end{pmatrix} = \delta(j'j) \begin{pmatrix} j \\ m & m' \end{pmatrix} = (-1)^{j+m} \delta(j'j)\, \delta(m', -m) \qquad (42)$$

where $\begin{pmatrix} j \\ mm' \end{pmatrix}$ corresponds to the Herring-Wigner metric tensor (cf. Ref. 2). Then, the introduction of Eq. (42) into Eq. (24) for the chain $SU_2 \supset U_1$ shows that the 3-aα symbol identifies to the 3-jm Wigner symbol $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$, i.e., $(-1)^{j_1+j_2+j_3} \overline{\mathrm{V}} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ in term of the $\overline{\mathrm{V}}$ Fano-Racah symbol, provided we choose $M(j_2 j_1, j_3) = (-1)^{2j_1}$. Such a choice

ensures that the 3-jm symbol is highly symmetrical under permutation of its columns.

In the SU_2 case, the above-mentioned $(6\text{-a})_{4\rho}$ and $(9\text{-a})_{6\rho}$ symbols may be chosen to coincide with the 6-j Wigner or $\overline{W}$ Fano-Racah symbol and the 9-j Wigner or X Fano-Racah symbol, respectively. This corresponds to

$$\begin{Bmatrix} j_1 & j_{23} & j \\ j_3 & j_{12} & j_2 \end{Bmatrix} = (-1)^{j_1+j_2+j_3+j} [(2j_{12}+1)(2j_{23}+1)]^{-1/2} \tag{43}$$

$$(j_1(j_2j_3)j_{23}jm \mid (j_1j_2)j_{12}j_3jm)$$

$$\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{Bmatrix} = [(2j_{12}+1)(2j_{34}+1)(2j_{13}+1)(2j_{24}+1)]^{-1/2} \tag{44}$$

$$((j_1j_3)j_{13}(j_2j_4)j_{24}jm|(j_1j_2)j_{12}(j_3j_4)j_{34}jm)$$

in terms of recoupling coefficients (cf., Eqs. (33) and (34)).

Finally, for $a \equiv k$, the ITS T^a of Sec. II coincides with the irreducible tensor operator $T^{(k)}$ introduced by Racah. We shall denote by T^k_q the $SU_2 \supset U_1$ components of $T^{(k)}$.

All the relations of Sec. II may be rewritten as familiar relations of angular momentum theory owing to the just described correspondance rules. For example, Eqs. (17) or (18) and (40) or (41) give

$$\mathfrak{D}^j(R)_{mm'}{}^* = (-1)^{m-m'} \mathfrak{D}^j(R)_{-m-m'} \tag{45}$$

$$(\tau'j'm' \mid T^k_q \mid \tau j m) = (-1)^{j'-m'} \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix} (\tau'j' \| T^k \| \tau j) \tag{46}$$

2 - The octahedral group

In the case of the octahedral group O (which is isomorphic to the symmetric group S_4), the label a may take only five values : $a \equiv A_1$, A_2, E, T_1, and T_2 in the Placzek-Mulliken notation. Further, we have $[A_1] = [A_2] = [E]/2 = [T_1]/3 = [T_2]/3 = 1$. The vectors $|\tau\ a\ \alpha)$ depend of course of the basis used. For example, it is frequent to use the Cartesian basis $\{|\ell\ a\ \alpha)\}$:

$$
\begin{aligned}
|0\ A_1\ a_1) &= |00) \\
|3\ A_2\ a_2) &= (1/\sqrt{2})|32) - (1/\sqrt{2})|3\text{-}2) \\
|2\ E\ \theta) &= |20) \\
|2\ E\ \varepsilon) &= (1/\sqrt{2})|22) + (1/\sqrt{2})|2\text{-}2) \\
|1\ T_1\ x) &= -(i/\sqrt{2})|11) + (i/\sqrt{2})|1\text{-}1) \\
|1\ T_1\ y) &= (1/\sqrt{2})|11) + (1/\sqrt{2})|1\text{-}1) \\
|1\ T_1\ z) &= i|10) \\
|2\ T_2\ x) &= (i/\sqrt{2})|21) + (i/\sqrt{2})|2\text{-}1) \\
|2\ T_2\ y) &= (1/\sqrt{2})|21) - (1/\sqrt{2})|2\text{-}1) \\
|2\ T_2\ z) &= -(i/\sqrt{2})|22) + (i/\sqrt{2})|2\text{-}2)
\end{aligned}
\qquad (47)
$$

defined in terms of the spherical basis vectors $|\ell\ m)$. The chemist recognizes that $|1\ T_1\ \alpha)$ with $\alpha \equiv x, y,$ and z transform under rotation like the orbitals p_x, $-p_y$, and p_z. Similarly, $|2\ E\ \alpha)$ with $\alpha \equiv \theta$ and ε transform like $d_{x^2 - y^2}$ and d_{z^2} while $|2\ T_2\ \alpha)$ with $\alpha \equiv x$, y, and z transform like d_{yz}, $-d_{zx}$, and d_{xy}. Note that the basis vectors defined by Eq. (47) behave very simply under the time reversal symmetry operation.

Here again, the label ρ is not necessary since O turns out to be a simply reducible (i.e., multiplicity-free and ambivalent) group. The coupling coefficients of O either in the Clebsch-Gordan or the 3-aα form have been calculated in various bases. Also, the recoupling coefficients of O appear in many publications and textbooks. (In the Griffith notation, the 3-aα, 6-a, and 9-a symbols of O are denoted as V, W, and X symbols.)

3 - The double octahedral group

The double or spinor octahedral group O^* is of importance for molecular aggregates with octahedral symmetry and involving an odd number of electrons. Besides the (vector or integer) IRC's A_1, A_2, E, T_1, and T_2 of O, the group O^* possesses three (spinor or half-integer) IRC's, viz., E', E'', and U' in the notation of Griffith with $[E'] = [E''] = [U']/2 = 2$. Here, complications arise since O^*, although ambivalent, is not multiplicity-free. In fact, we have $U' \otimes U' = A_1 \oplus A_2 \oplus E \oplus 2T_1 \oplus 2T_2$ so that multiplicity labels are required for the coupling coefficients involving the triads $(U'U'T_1)$ and $(U'U'T_2)$. The coupling and recoupling coefficients of O^* have been given by many authors with unfortunately different phase conventions. Among the works about the coupling and recoupling coefficients of O and O^*, we must mention the pioneer works of Refs. 4-7. It is hoped that the combination of various aspects of the works of Refs. 4-34 and of other works could lead to standardized coupling and recoupling coefficients of (O and) O^*.

IV - SU_2 IN A $SU_2 \supset G$ BASIS

We now consider the double group G of a point (proper) rotation group. Rather than considering G as an isolated group, we explicitly use the fact that G is a subgroup of SU_2. This leads to the investigation of the WRa of SU_2 in a $SU_2 \supset G$ basis. In this section, we use the labels Γ and γ in place of the labels of type a and α for the group G, respectively.

1 - The restriction of SU_2 to G

Each IRC j of SU_2 can be decomposed into a direct sum of

IRC's of G :

$$j = \bigoplus_{\Gamma} \sigma(\Gamma|j)\Gamma \tag{48}$$

where

$$\sigma(\Gamma|j) = |G|^{-1} \int_G dR\, \chi^{\Gamma}(R)^* \chi^{j}(R) \tag{49}$$

stands for the multiplicity of the IRC Γ of G in j. In terms of unitary matrix representations, this means that

$$\mathfrak{D}^{j} \sim \bigoplus_{\Gamma} \sigma(\Gamma|j)\, \mathfrak{D}^{\Gamma} \tag{50}$$

In other words, there exists a unitary matrix U^j such that

$$(U^j)^{\dagger}\, \mathfrak{D}^{j}(R)\, U^{j} = \bigoplus_{\Gamma} \sigma(\Gamma|j)\, \mathfrak{D}^{\Gamma}(R) \tag{51}$$

holds for any R in G. This leads to

$$\sum_{mm'} (jm|ja\Gamma\gamma)^* \mathfrak{D}^{j}(R)_{mm'} (jm'|ja'\Gamma'\gamma') = \delta(a'a)\,\delta(\Gamma'\Gamma)\, \mathfrak{D}^{\Gamma}(R)_{\gamma\gamma'} \tag{52}$$

$$\mathfrak{D}^{j}(R)_{mm'} = \sum_{a\Gamma\gamma\gamma'} (jm|ja\Gamma\gamma)\, \mathfrak{D}^{\Gamma}(R)_{\gamma\gamma'} (jm'|ja\Gamma\gamma')^* \tag{53}$$

for any R in G. In Eqs. (52) and (53), $(jm|ja\Gamma\gamma)$ denotes an element of the matris U^j :

$$(jm|ja\Gamma\gamma) = (U^j)_{m,a\Gamma\gamma} \tag{54}$$

The label a (cf., the column index $a\Gamma\gamma$ of U^j) is a branching multiplicity label indispensable when Γ appears more than once in j. Note that the unitary property of the matrix U^j corresponds to R = E, the unit element of G, in Eqs. (52) and (53) :

$$\sum_{m} (jm|ja\Gamma\gamma)^{*} (jm|ja'\Gamma'\gamma') = \delta(a'a)\,\delta(\Gamma'\Gamma)\,\delta(\gamma'\gamma) \tag{55}$$

$$\sum_{a\Gamma\gamma} (jm|ja\Gamma\gamma)\,(jm'|ja\Gamma\gamma)^{*} = \delta(m'm) \tag{56}$$

Observe that Eqs. (52) and (53) are not sufficient for determining the reduction coefficients $(jm|ja\Gamma\gamma)$ once the irreducible representation matrices of G and SU_2 are known since the coefficients

$$(jm|jb\Gamma\gamma) = \sum_{a} (jm|ja\Gamma\gamma)\,M_{ab} \tag{57}$$

where M is an arbitrary unitary matrix satisfy Eqs. (52) and (53) with the replacement $a \to b$. Nevertheless, Eqs. (52) and (53) lead to systems that may be useful for the calculation of the $(jm|ja\Gamma\gamma)$.

2 - Irreducible tensorial sets

From the ITS of vectors $\{|\tau jm) : m = -j(1)j\}$ associated to $\mathfrak{D}^{j}$, we define

$$|\tau ja\Gamma\gamma) = \sum_{m} |\tau jm)\,(jm|ja\Gamma\gamma) \tag{58}$$

Equation (53) allows us to show

$$P_R|\tau ja\Gamma\gamma) = \sum_{\gamma'} |\tau ja\Gamma\gamma')\,\mathfrak{D}^{\Gamma}(R)_{\gamma'\gamma} \tag{59}$$

for any R in G. Similarly, from the ITS of operators $\{T^{k}_{q} : q = -k(1)k\}$ associated to $\mathfrak{D}^{k}$, we define

$$T^{ka\Gamma}_{\gamma} \quad \text{or} \quad T^{k}_{a\Gamma\gamma} = \sum_{q} T^{k}_{q}\,(kq|ka\Gamma\gamma) \tag{60}$$

so that

$$P_R \, T^{k\,a\,\Gamma}_{\gamma} \, P_R^{-1} = \sum_{\gamma'} T^{k\,a\,\Gamma}_{\gamma'} \, \mathfrak{D}^{\Gamma}(R)_{\gamma'\gamma} \tag{61}$$

holds for any R in G.

At this point, it is important to remark that Eqs. (58) and (60) provide us with ITS' both for SU_2 and G. Indeed, $\{|\tau\, j\, a\, \Gamma\, \gamma) : \gamma \text{ ranging}\}$ is an ITS of vectors spanning the matrix representation $\mathfrak{D}^{\Gamma}$ of G while $\{|\tau\, j\, a\, \Gamma\, \gamma) : a\Gamma\, \gamma \text{ ranging}\}$ is an ITS of vectors spanning the matrix representation D^j of SU_2 defined by

$$D^j(R)_{a\Gamma\gamma,\, a'\Gamma'\gamma'} = \sum_{mm'} (jm|j\,a\,\Gamma\,\gamma)^* \, \mathfrak{D}^j(R)_{mm'} \, (jm'|j\,a'\Gamma'\gamma') \tag{62}$$

for any R in SU_2. A similar remark applies to $\{T^{k\,a\,\Gamma}_{\gamma} : \gamma \text{ ranging}\}$ and $\{T^{k}_{a\Gamma\gamma} : a\Gamma\gamma \text{ ranging}\}$.

3 - Wigner-Eckart theorems

As an important consequence of the latter two remarks, we may apply the Wigner-Eckart theorem either for the group SU_2 in a $SU_2 \supset G$ basis or for the group G in a $G \subset SU_2$ basis. For G in a $G \subset SU_2$ basis, Eq. (40) gives

$$(\tau_1 j_1 a_1 \Gamma_1 \gamma_1 | T^{k\,a\,\Gamma}_{\gamma} | \tau_2 j_2 a_2 \Gamma_2 \gamma_2) = \sum_{\rho} (\tau_1 j_1 a_1 \Gamma_1 || T^{ka\Gamma} || \tau_2 j_2 a_2 \Gamma_2)_{\rho} \sum_{\Gamma_1' \gamma_1'} \begin{pmatrix} \Gamma_1' & \Gamma_1 \\ \gamma_1' & \gamma_1 \end{pmatrix} \begin{pmatrix} \Gamma & \Gamma_2 & \Gamma_1' \\ \gamma & \gamma_2 & \gamma_1' \end{pmatrix}_{\rho}^{*} \tag{63}$$

For SU_2 in a $SU_2 \supset G$ basis, we can combine Eqs. (41), (58), and (60) to obtain the compact formula

$$(\tau_1 j_1 a_1 \Gamma_1 \gamma_1 | T^{k}_{a\Gamma\gamma} | \tau_2 j_2 a_2 \Gamma_2 \gamma_2) = (\tau_1 j_1 || T^{k} || \tau_2 j_2) f \begin{pmatrix} j_1 & j_2 & k \\ a_1 \Gamma_1 \gamma_1 & a_2 \Gamma_2 \gamma_2 & a \Gamma \gamma \end{pmatrix} \tag{64}$$

where the f symbol is defined by[13]

$$f\begin{pmatrix} j_1 & j_2 & k \\ a_1\Gamma_1\gamma_1 & a_2\Gamma_2\gamma_2 & a\Gamma\gamma \end{pmatrix} = (-1)^{2k}(2j_1+1)^{-1/2}\ (j_2 k a_2\Gamma_2\gamma_2 a\Gamma\gamma | j_1 a_1\Gamma_1\gamma_1)^* \qquad (65)$$

in function of the CGc

$$(j_1 j_2 a_1\Gamma_1\gamma_1 a_2\Gamma_2\gamma_2 | ja\Gamma\gamma) = \sum_{m_1 m_2 m} (j_1 m_1 | j_1 a_1\Gamma_1\gamma_1)^*$$

$$(j_2 m_2 | j_2 a_2\Gamma_2\gamma_2)^*\ (j_1 j_2 m_1 m_2 | jm)(jm | ja\Gamma\gamma) \qquad (66)$$

of SU_2 in a $SU_2 \supset G$ basis.

There are many advantages to use Eq. (64) rather than Eq. (63). In Eq. (63), both the reduced matrix elements and the coupling coefficients (cf., the 2-aα and $(3\text{-}a\alpha)_\rho$ symbols) depend of the symmetry group G. Furthermore, the factorization offered by Eq. (63) is not complete in view of the summation over the multiplicity label ρ. On the other side, the matrix element given by Eq. (64) factorizes in two parts : a coupling coefficient (cf., the f symbol) for the chain $SU_2 \supset G$ and a reduced matrix element which does not depend of the group G. This maximal factorization takes place even in the case where G is not multiplicity-free. The reduced matrix elements in Eq. (64) applied to complex systems either are obtainable from tables or can be calculated from Racah's method in terms of recoupling coefficients of SU_2, coefficients of fractional parentage, and elementary reduced matrix elements. The main calculation to do when dealing with Eq. (64) most of the time concerns the geometrical coefficient f( ), a quantity which is independent of the additional quantum numbers τ_1 and τ_2 and which remains invariant when the tensor operator $\mathbf{T}^k$ is replaced by any tensor operator $\mathbf{U}^k$.

The calculation of the coefficients f( ) defined by Eqs. (65) and (66) touches a simple problem of symmetry adaptation. In fact, the

determination of the symmetry adapted CGc's (66) require the knowledge of the reduction coefficients (54). These reduction coefficients are the expansion coefficients of symmetry adapted functions (cf., Eq. (58)) or symmetry adapted operators (cf., Eq. (60)) so that their calculation may be achieved by numerous means (resolution of linear systems like (52) or (53), projection operator techniques, ...).

4 - The $\bar{f}$ symbol

Equation (65) shows that the behaviour of the f symbol under the interchange of its first and second columns is not easy to describe. The f symbol may be symmetrized owing to the introduction of the 1-j a Γ γ symbol[13]

$$\begin{pmatrix} & j & \\ a\,\Gamma\,\gamma & & a'\,\Gamma'\,\gamma' \end{pmatrix} = \sum_{mm'} (jm|ja\,\Gamma\,\gamma)^* \begin{pmatrix} j \\ m \end{pmatrix} \begin{pmatrix} j \\ m' \end{pmatrix} (jm'|ja'\Gamma'\gamma')^* \qquad (67)$$

where the 1-jm symbol is defined by Eq. (42). The $\bar{f}$ or 3-j a Γ γ symbol defined through[13]

$$\bar{f}\begin{pmatrix} j_1 & j_2 & j_3 \\ a_1\,\Gamma_1\,\gamma_1 & a_2\,\Gamma_2\,\gamma_2 & a_3\,\Gamma_3\,\gamma_3 \end{pmatrix} = \sum_{a_4\Gamma_4\gamma_4} \begin{pmatrix} j_3 \\ a_3\,\Gamma_3\,\gamma_3 & a_4\,\Gamma_4\,\gamma_4 \end{pmatrix} f\begin{pmatrix} j_3 & j_2 & j_1 \\ a_4\,\Gamma_4\,\gamma_4 & a_2\,\Gamma_2\,\gamma_2 & a_1\,\Gamma_1\,\gamma_1 \end{pmatrix}^* \qquad (68)$$

then exhibits a high (permutational) symmetry since a simple development of Eq. (68) leads to

$$\bar{f}\begin{pmatrix} j_1 & j_2 & j_3 \\ a_1\,\Gamma_1\,\gamma_1 & a_2\,\Gamma_2\,\gamma_2 & a_3\,\Gamma_3\,\gamma_3 \end{pmatrix} = \sum_{m_1m_2m_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \prod_{i=1}^{3} (j_i m_i | j_i a_i \Gamma_i \gamma_i)^* \qquad (69)$$

For $G \equiv U_1$ the $\bar{f}$ symbol and the 1-j a Γ γ symbol reduce to the 3-jm Wigner symbol and to the 1-jm Herring-Wigner symbol,

respectively. The 1-j a Γ γ and $\bar{f}$ symbols are thus 2-aα and 3-aα symbols as defined in Sec. II (with a → j and α → a Γ γ), respectively, for the group SU_2 in a $SU_2 \supset G$ basis. The properties (existence conditions, selection rules, symmetry properties, orthogonality properties, ...) of the $\bar{f}$ (and f) symbols can be deduced from the ones of the 3-jm symbols and the U^j matrices and have been discussed at length elsewhere.[13,14] Let us only mention that, by applying a lemma due to Racah,[1] the $\bar{f}$ symbol may be developed as a linear combination of $(3\text{-}\Gamma\gamma)_\rho$ symbols of G according to

$$\bar{f}\begin{pmatrix} j_1 & j_2 & j_3 \\ a_1\Gamma_1\gamma_1 & a_2\Gamma_2\gamma_2 & a_3\Gamma_3\gamma_3 \end{pmatrix} = \sum_\rho \bar{f}\left(\!\!\left(\begin{matrix} j_1 & j_2 & j_3 \\ a_1\Gamma_1 & a_2\Gamma_2 & a_3\Gamma_3 \end{matrix} \right)\!\!\right)_\rho \begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix}_\rho \tag{70}$$

where the reduced coefficient $\bar{f}$ (( )) is independent of γ_1, γ_2, and γ_3.

We are now in position to enunciate the correspondence rules to pass from the WRa of SU_2 in a $SU_2 \supset U_1$ basis (i.e., the $\{jm\}$ scheme) to the WRa of SU_2 in a $SU_2 \supset G$ basis (i.e., the $\{j\, a\Gamma\gamma\}$ scheme) : All the m-dependent quantities are replaced by the corresponding $a\Gamma\gamma$-dependent quantities while the basis-independent quantities (like the 6-j and 9-j symbols) are unchanged. More precisely, we have

$$\mathfrak{D}^j(R)_{mm'} \longrightarrow D^j(R)_{a\Gamma\gamma,a'\Gamma'\gamma'}$$

$$(j_1 j_2 m_1 m_2 | jm) \longrightarrow (j_1 j_2 a_1\Gamma_1\gamma_1 a_2\Gamma_2\gamma_2 | j\, a\Gamma\gamma)$$

1-jm symbol ⟶ 1-j a Γ γ symbol

3-jm symbol ⟶ $\bar{f}$ symbol (71)

3(n-1)-j symbol ⟶ 3(n-1)-j symbol

$$|\tau\, j\, m) \longrightarrow |\tau\, j\, a\, \Gamma\, \gamma)$$

$$T^k_q \longrightarrow T_{a\,\Gamma\,\gamma}{}^k$$

V - G IN A $G \subset SU_2$ BASIS

1 - The general case

Equations (12)-(15) or their analogs with V symbols have been used in numerous works for calculating coupling coefficients of subgroups of SU_2. (Following Griffith, the $(3\text{-}a\,\alpha)_\beta$ symbols of a group of molecular interest are referred to as V symbols.) As a pending part of Sec. IV, we now describe an alternative method for calculating the V coefficients of a subgroup G of SU_2 as renormalized $\bar{f}$ coefficients of the chain $SU_2 \supset G$. This method combines three basic ingredients : the concept of quasi angular momentum, the definition of the $\bar{f}$ symbol, and the renormalization techniques scattered in various works amongst Refs. 4-34. For the purpose of simplicity, we shall limit ourselves to a multiplicity-free group G but it should be noted that the method may be extended to an arbitrary subgroup of SU_2.

Given the IRC Γ of G, let $\mathfrak{f}(\Gamma)$ or simply $\mathfrak{f}$ be the IRC of SU_2 that contains Γ once and only once. Thus, $\mathfrak{f}$ is the smallest value of j for which $\sigma(\Gamma|j) = 1$. (In Ref. 10, $\mathfrak{f}$ is called a quasi angular momentum.) In the (multiplicity-free) case where the identity IRC of G appears only once in the triple direct product $\Gamma_1 \otimes \Gamma_2 \otimes \Gamma_3$, there is no need for the internal multiplicity label ρ in the 3-$\Gamma\gamma$ or V symbol. Therefore, let us put

$$V\begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix} = x(\Gamma_1\Gamma_2\Gamma_3)\,\bar{f}\begin{pmatrix} \mathfrak{f}_1 & \mathfrak{f}_2 & \mathfrak{f}_3 \\ \Gamma_1\gamma_1 & \Gamma_2\gamma_2 & \Gamma_3\gamma_3 \end{pmatrix}$$

$$\left[\sum_{\gamma_1\gamma_2\gamma_3} \left|\bar{f}\begin{pmatrix} \mathfrak{f}_1 & \mathfrak{f}_2 & \mathfrak{f}_3 \\ \Gamma_1\gamma_1 & \Gamma_2\gamma_2 & \Gamma_3\gamma_3 \end{pmatrix}\right|^2\right]^{-1/2} \qquad (72)$$

where $x(\Gamma_1\Gamma_2\Gamma_3)$ is an arbitrary phase factor that depends on Γ_1, Γ_2, and Γ_3 only. It can be verified by repeated application of Eq. (70) that the V symbol defined by Eq. (72) satisfies Eqs. (26) and (27) for the group G. Consequently, the V symbol is nothing but a 3-$\Gamma\gamma$ symbol for the group G

compatible with the choice implicitly assumed through Eq. (69) with $j = \hat{j}$ for the matrix representations $\mathcal{D}^{\Gamma}$.

For the sake of calculational simplicity with Eq. (72), it should be noticed that

$$\sum_{\gamma_1\gamma_2\gamma_3} \left| \bar{f} \begin{pmatrix} \hat{j}_1 & \hat{j}_2 & \hat{j}_3 \\ \Gamma_1\gamma_1 & \Gamma_2\gamma_2 & \Gamma_3\gamma_3 \end{pmatrix} \right|^2 = [\Gamma_i] \sum_{\substack{\text{all } \gamma_k \\ \text{except } \gamma_i}} \left| \bar{f} \begin{pmatrix} \hat{j}_1 & \hat{j}_2 & \hat{j}_3 \\ \Gamma_1\gamma_1 & \Gamma_2\gamma_2 & \Gamma_3\gamma_3 \end{pmatrix} \right|^2 \tag{73}$$

for $i = 1$, 2, or 3. In addition, if two of the three Γ's equal two of the three j's, the right-hand side of Eq. (73) takes a simple value and Eq. (72) may be further simplified. For instance, in the case $\hat{j}_1 \equiv \Gamma_1$ and $\hat{j}_2 \equiv \Gamma_2$, Eq. (72) reduces to

$$V\begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix} = x\,(\Gamma_1\Gamma_2\Gamma_3)\ \bar{f} \begin{pmatrix} j_1 & j_2 & j_3 \\ \Gamma_1\gamma_1 & \Gamma_2\gamma_2 & \Gamma_3\gamma_3 \end{pmatrix} [\Gamma_3]^{-1/2}\ (2j_3+1)^{1/2} \tag{74}$$

The main advantages of the method based on Eqs. (72)-(74) for calculating the V coefficients of G may be seen to be the following. First, the calculation is easy in the sense that the V coefficients are actually deduced from a minimal set of $\bar{f}$ coefficients which are readily calculated (by hand or with a pocket calculator) from Eq. (69). The V coefficients of the group G thus obtained are finally simple linear combinations of 3-jm coefficients of the chain $SU_2 \supset U_1$. Second, such a method allows to work with a basis of chemical interest. In this respect, we may use in Eq. (69) reduction coeffi - cients $(jm|ja\Gamma\gamma)$ corresponding to Cartesian p, d, and f (spin-) orbitals or corresponding to a chain of groups (for instance, the tetragonal chain $SU_2 \supset O^* \supset D_4^* \supset D_2^*$ or the trigonal chain $SU_2 \supset O^* \supset D_3^* \supset C_3^*$). Third, it is possible to transfer some of the features (formulas, symmetry properties, ...) of the 3-jm symbol of the standard chain $SU_2 \supset U_1$ to the V symbol of G.

For example, the permutational symmetry properties of the V symbol can be chosen to be essentially the ones of the 3-jm symbol. In fact, by chosing $x(\Gamma_1\Gamma_2\Gamma_3)$ invariant under the 3 ! permutations of its arguments, the V symbol given by Eqs. (72)-(74) is multiplied by $(-1)^{j_1(\Gamma_1)+j_2(\Gamma_2)+j_3(\Gamma_3)}$ under an odd permutation of its columns so that it is invariant under an even permutation.

2 - Application to O

As an illustration, we consider the case where G stands for the double octahedral group O^*. The restriction of SU_2 to O^* immediately shows that

$$j(A_1) = 0, \quad j(A_2) = 3, \quad j(E) = 2, \quad j(T_1) = 1, \quad j(T_2) = 2$$
$$j(E') = 1/2, \quad j(E'') = 5/2, \quad j(U') = 3/2 \qquad (75)$$

In view of the permutational symmetry properties of the V symbol, they are a priori 39 independent V coefficients to be calculated for the group O. The vectors $|j\Gamma\gamma)$ required for calculating these coefficients are given by Eq. (47). The 39 independent V coefficients are then easily calculated from Eqs. (47), (69), and (72)-(75). They are of course all real if we take i = 1 in Eq. (47). In the case $i = \sqrt{-1}$, it is possible to decrease the number of independent V coefficients by conveniently choosing the phase factors $x(\Gamma_1\Gamma_2\Gamma_3)$. In this regard, by taking $i = \sqrt{-1}$ and $x(\Gamma_1\Gamma_2\Gamma_3) = 1$ except $x(E\,T_2\,T_2) = x(T_1\,T_1\,T_1) = x(T_1\,T_1\,T_2) = x(T_2\,T_2\,T_2) = -1$, the reader will verity that Eqs. (47), (69), and (72)-(75) exactly lead to the (real) numerical values obtained by Griffith[6] for his V coefficients of O in his real tetragonal component system. The V coefficients thus obtained satisfy the so-called p^n isomorphism property[6] that corresponds to the special choice $\mathcal{D}^{T_2}(R) = \chi^{A_2}(R)\,\mathcal{D}^{T_1}(R)$ for any R in O, a choice often done in the study of the symmetric group $S_4 \sim O$ since the IRC [31] of S_4 (i.e., T_1 of O) is conjugated to the IRC [211] of S_4 (i.e., T_2 of O).

It is to be mentioned that, should we have taken the basis $\{|\ell\Gamma(O)\,\Gamma(D_4)\,\Gamma(D_2))\}$:

$$|0\,A_1\,A_1\,A) = |0\,A_1\,a_1)$$

$$|3\,A_2\,B_1\,A) = |3\,A_2\,a_2)$$

$$|2\,E\,A_1\,A) = |2\,E\,\theta),\quad |2\,E\,B_1\,A) = |2\,E\,\epsilon) \tag{76}$$

$$|1\,T_1\,A_2\,B_1) = |1\,T_1\,z),\quad |1\,T_1\,E\,B_2) = -|1\,T_1\,y),\quad |1\,T_1\,E\,B_3) = |1\,T_1\,x)$$

$$|2\,T_2\,B_2\,B_1) = |2\,T_2\,z),\quad |2\,T_2\,E\,B_2) = |2\,T_2\,y),\quad |2\,T_2\,E\,B_3) = |2\,T_2\,x)$$

adapted to the chain $R_3 \supset O \supset D_4 \supset D_2$, it would have been impossible to fix the phase factors $x(\Gamma_1\,\Gamma_2\,\Gamma_3)$ in such a way that the V coefficients for O obey the p^n isomorphism property. This reflects the fact that the p^n isomorphism property is incompatible with an adaptation to the symmetry D_4. More precisely, the standardization of the irreducible representation matrices associated with the IRC E of D_4 is incompatible with a choice of the vectors $|\ell\,\Gamma(O)\,\Gamma(D_4)\,\Gamma(D_2))$ such that $\mathfrak{D}^{T_2}(R) = \chi^{A_2}(R)\ \mathfrak{D}^{T_2}(R)$ for any R in O.

The reader will note that each of the V coefficients calculated by using Eqs. (69) and (72)-(75) in conjunction with the data of either Eq. (47) or Eq. (76) reduces (up to a multiplicative factor) to solely one 3-jm coefficient for the chain $R_3 \supset C_\infty$. We thus foresee that some properties of certain 3-jm symbols for the chain $SU_2 \supset U_1$ may be derived by looking at some properties induced by a subgroup of SU_2 (rather than a group that contains SU_2 as subgroup). For example, let us consider the coefficient $V\begin{pmatrix} A_2 A_2 E \\ a_2 a_2 \theta \end{pmatrix}$ for the group O. Equation (72) with the data of Eq. (47) leads to

$$V\begin{pmatrix} A_2 & A_2 & E \\ a_2 & a_2 & \theta \end{pmatrix} \tilde{=} \bar{f}\begin{pmatrix} 3 & 3 & 2 \\ A_2a_2 & A_2a_2 & E\,\theta \end{pmatrix} = -\begin{pmatrix} 3 & 3 & 2 \\ -2 & 2 & 0 \end{pmatrix} \qquad (77)$$

On the other hand, the numerical value of the $\bar{f}$ symbol being considered is zero since the triple Kronecker product $A_2 \otimes A_2 \otimes E$ does not contain the identity IRC A_1 of O. As a consequence, the 3-jm symbol $\left(\begin{smallmatrix} 3 & 3 & 2 \\ -2 & 2 & 0 \end{smallmatrix}\right)$ for the chain $R_3 \supset C_\infty$ is seen to be zero (owing to a selection rule for O) in spite of the fact that the (trivial and Regge) symmetry properties relative to $R_3 \supset C_\infty$ do not impose such a result.

VI - DISCUSSION

The interest for quantum chemistry of symmetry adapted functions and symmetry adapted operators has been recognized for a long time. As a matter of fact, theoretical chemistry deals with physical systems which are left invariant under point symmetry groups. Therefore, the consideration of state functions and operators spanning irreducible representations of a point symmetry group G is of paramount importance for the calculation (via the Wigner-Eckart theorem for example) of matrix elements. Such calculations are fully standardized through the Wigner-Racah algebra of G or its double group G^*. (The complete description of the electronic properties of a molecular system invariant under a group G requires the introduction of the double group G^* of G when the total number of electrons of the system is odd.) In such an approach the group G or G^* is considered as an isolated group. This line of thought corresponds to the developments of Sec. II and the examples of Sec. III. It has been largely used in ligand-field theory especially in connection with the strong-field formalism for compounds involving $3d^N$ ions.[4,6,35]

However, the group G is a subgroup of the three-dimensional proper and improper rotation group (isomorphic to the orthogonal group in three dimensions O_3), so that instead of considering G as an entity we may

consider it as being embedded in O_3. Indeed, it is sufficient from a formal point of view to visualize G as a subgroup of the three-dimensional proper rotation group R_3 (isomorphic to the special orthogonal group in three dimensions SO_3) due to the fact that each point symmetry group is isomorphic to a proper rotation group or is isomorphic to the direct product of a proper rotation group times Z_2 (the abstract group of order two). This leads to the introduction of chains of the type $R_3 \supset G$ or $SU_2 \supset G^*$ depending whether we have to describe electronic properties of a system with an even or an odd number of electrons. (The special unitary group in two dimensions SU_2 is isomorphic to the double group of R_3.)

Since in Nature we rarely have a system with a perfect symmetry, it is often necessary to consider in addition to the invariance group G an invariance subgroup of G for a more realistic description of the system. Furthermore, it may be useful for the purpose of classifying the physical states and interactions to introduce when possible a super group, subgroup of R_3 and having G as a subgroup. This leads to chains of the type $SU_2 \supset G_1 \supset G_2 \supset G_3$. This nonindividualistic or family approach (in contradistinction to the case where each group is considered as an entity) presents several advantages. From a physical point of view, some of the links of the considered chain correspond to a certain degree of approximation, in the sense that these links are the double groups of groups describing descent in symmetry. In this respect, the reduction $SU_2 \rightarrow G_1 \rightarrow G_2 \rightarrow G_3$ clearly describes the evolution of the system when its symmetry is lowered. From a mathematical point of view, the above discussed links together with the remaining ones are very useful for classifying the physical states and interactions. Such a classification is partially achieved by making use of irreducible representations classes for the different groups in the chain $SU_2 \supset G_1 \supset G_2 \supset G_3$. Consequently, the calculation of matrix elements is greatly simplified by the selection rules on each group of the chain under consideration. A further important computational advantage is the following : the matrix of an operator invariant under R_3 (as for example the interelectronic repulsion operator) is easily deduced from well-known formulas or tables or can be set up by using standard programs.

The Wigner-Racah algebra of a chain of the type $SU_2 \supset G_1 \supset G_2 \supset G_3$ is deducible by simple adaptation of the notation from the one described in Sec. IV for the group SU_2 in a $SU_2 \supset G$ basis. The consideration of the Wigner-Racah algebra of SU_2 in a $SU_2 \supset G_1 \supset G_2 \supset G_3$ basis has been successfully used in ligand-field theory and related matters (cf., Refs. 8, 11, 13, 14, and 36-40) as well as in vibrational-rotational spectroscopy of small molecules and polyatomic ions in crystals (cf., Refs. 9, 41, and 42). In particular, the f coefficients for the chain $SU_2 \supset G$ play a central role in ligand-field theory especially in the weak-field formalism applied to partly filled shell ions embedded in a surrounding of symmetry G.[13,14,40] This has been clearly showed in the investigation of luminescence spectra of rare earth ions in crystals (cf., for example Ref. 37). The f coefficients can be also used in the spin-Hamiltonian formalisms.[38] Finally, they occur in photoelectron spectroscopy both for the valence band and the core levels of partly filled shell ions in symmetry G.[39]

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