THE IMPACT OF GIULIO RACAH ON CRYSTAL- AND LIGAND-FIELD THEORIES

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Abstract

This paper focuses on the impact of Racah on crystal- and ligand-field theories, two branches of molecular physics and condensed matter physics (dealing with ions embedded in aggregates of finite symmetry). The role of Racah and some of his students in developing a symmetry-adapted weak-field model for crystal-field theory is examined. Then, we discuss the extension of this model to a generalized symmetry-adapted weak-field model for ligand-field theory. Symmetry considerations via the use of the Wigner-Racah algebra for chains of type $SU(2) \supset G$ is essential for these weak-field models. Therefore, the basic ingredients for the Wigner-Racah algebra of a finite or compact group are reviewed with a special attention paid to the $SU(2)$ group in a $SU(2) \supset G$ basis. Finally, as an unexpected application of nonstandard $SU(2)$ bases, it is shown how $SU(2)$ bases adapted to the cyclic group allow to build bases of relevance in quantum information.

1 Introduction

The legacy of Giulio Racah (Firenze, 1909-1965) stems mainly from his four papers *Theory of complex spectra* published between 1942 and 1949 [1, 2, 3, 4], his notes on group-theoretical methods in spectroscopy based on lectures given at the Institute for Advanced Study in Princeton in 1951 [5, 6], and his book on irreducible tensorial sets written in collaboration with his cousin Ugo Fano [7].

It was the purpose of the first paper of his famous series [1, 2, 3, 4] to substitute to the numerical methods of Slater, Condon and Shortley general methods more conformable to the Dirac representation of state vectors. The main achievements realized in [1, 2, 3, 4, 5, 6, 7] deal with irreducible tensor methods, Wigner-Racah algebra (or Racah-Wigner algebra or Racah algebra, a concept to be precisely defined in Section 3) and group-theoretical methods involving chains of Lie groups. More precisely, let us mention the following important contributions.

- The development of the algebra of coupling and recoupling coefficients for the $SU(2)$ group in a $SU(2) \supset U(1)$ basis, with introduction of the V and $\overline{V}$ *functions* (the $\overline{V}$ symbol is identical to the $3-jm$ Wigner symbol up to a permutation of its columns) and of the W, $\overline{W}$ and X *functions* (the $\overline{W}$ and X symbols are identical to the $6-j$ and $9-j$ Wigner symbols, respectively).

- The introduction of the concept of a $SU(2)$ irreducible *tensor operator* that generalizes the notion of a vector operator and the generalization to tensor operators of the Wigner-Eckart theorem for vector operators.

- The introduction of the notion of a *unit tensor operator*, the matrix elements of which in a $SU(2) \supset U(1)$ basis are nothing but Clebsch-Gordan coefficients (up to a multiplicative factor), with the advantage that any tensor operator is proportional to a unit tensor operator.

- The introduction of the concept of *seniority* which is related to the state labeling problem.

- The development of the notion of *coefficients of fractional parentage*, previously introduced by Goudsmit and Bacher, which make it possible to develop a n–particle wavefunction in terms of $(n-1)$–particle wavefunctions.

- The introduction of *chains of Lie groups*, involving both invariance and classification groups, for characterizing state vectors and interactions involved in spectroscopic problems. To implement the use of chains of groups, Racah introduced a *factorization lemma* and developed the notion of a *complete set of commuting operators* (involving Cartan operators, invariant or Casimir operators and labeling operators) in a group-theoretical context.

The series of seminal works [1, 2, 3, 4, 5, 6, 7] opened the way for many applications by Racah himself, his students and a large part of the community of scientists working in atomic and nuclear spectroscopy (see the list of Racah's publications in [8]). In particular, the methods of Racah were popularized by Judd [9], Wybourne [10], and Condon and Odabaşi [11] in atomic physics and by de-Shalit and Talmi [12] in nuclear physics (see also [13, 14, 15, 16] for recent developments in nuclear and molecular physics). The basic concepts introduced and/or developed by Racah in his pioneer works were also of considerable importance in molecular and condensed matter physics. More specifically, these works stimulated an enormous quantity of

developments in vibration-rotational spectroscopy of molecules and in crystal- and ligand-field theories as will be shown below.

We shall be concerned here with the impact of Racah on crystal- and ligand-field theories, two theories which deal with optical, magnetic and thermal properties of ions embedded in molecular, condensed matter or biological surroundings. Racah never published papers about these theories. However, he was interested in molecular physics as shown by the fact that he published in 1943 a short note on the structure of the $Mo(CN)_8^{4-}$ complex ion [17]. His interest for molecular physics and the physics of ions in crystals was reinforced and stimulated by a seminar given by his colleague Willy Low in the Department of Physics of the Hebrew University of Jerusalem in 1956 [18, 19, 20]. The seminar was devoted to the role of crystalline fields on the optical spectra of transition-metal ions (like Ni^{2+} and Co^{2+}) in crystals. Racah became very much interested in this research subject and decided to guide students in this direction. His idea was to combine his irreducible tensor methods with the group-theoretical methods largely used in crystal-field theory (but principally applied in those times to a qualitative explanation of the level splitting for a given ion embedded in a finite symmetry surrounding). Along this line, Racah and Low directed two graduate students, Schoenfeld who studied the case of the d^2 and d^3 configurations in cubic symmetry [21] and Rosengarten who dealt with the case of d^4 and d^5 configurations in the same symmetry [22]. Then, Racah asked another student, Flato, to work out the more involved case of the d^2 and d^3 configurations in trigonal and tetragonal symmetries [23]. Five years after having completed his thesis, the material contained in Flato's thesis was still of such an interest that he was asked to publish it (for the main part) [24] (see also [25]). Research in that direction continued with a general formalism and a symmetry-adapted weak-field model developed by the present author in his thesis prepared under the guidance of Flato [26, 27, 28].

It is one of the aims of the present review to show how Racah directly and indirectly contributed to the penetration in crystal- and ligand-field theories of the tools he originally developed for atomic and nuclear spectroscopy. Another aim of this article is to show how the Wigner-Racah algebra for a group of molecular or crystallographic interest can be deduced from the one of $SU(2)$ in a nonstandard basis. To a large extent, this paper constitutes a brief review of the methods and models used in crystal- and ligand-field theories as well as a pedestrian presentation of the Wigner-Racah algebra for a chain of groups involving finite and/or compact groups. As an application of the $SU(2) \supset G$ chain, where G is a cyclic group, a brief contact is established with quantum information, a field of considerable interest in the present days.

The material in this paper is organized as follows. Section 2 deals with crystal- and ligand-field theories. The basic ingredients for the Wigner-Racah algebra of a finite or compact group together with some illustrative examples are given in Section 3. Section 4 is devoted to a short incursion in quantum information via the use of specific chains of type $SU(2) \supset G$.

Most of the notations are standard. The star denotes complex conjugation, δ_{ab} the Kronecker delta symbol of a and b, and $A^\dagger$ the adjoint of the operator A. We use a notation of type $|\psi)$

(as in Racah's papers), or $|\psi\rangle$ (as in quantum information), for a vector in an Hilbert space and we denote $\langle\phi|\psi\rangle$ and $|\phi\rangle\langle\psi|$ respectively the inner and outer products of the vectors $|\psi\rangle$ and $|\phi\rangle$. Specific notations on group theory shall be introduced later.

2 Crystal- and ligand-field theories

2.1 Generalities

Crystal- and ligand-field theories deal with the description and interpretation of electronic and magnetic properties (optical spectra, electron paramagnetic resonance spectra, photo-electron spectra, etc.) of a partly-filled shell ion in a molecular, condensed matter or biological environment. Crystal-field theory (based on the use of atomic orbitals) goes back to the end of the twenties with the seminal work by Bethe [29] and was applied to the spectroscopy of ions in solids in the early days of quantum mechanics. It is only in the fifties that ligand-field theory (based on the use of molecular orbitals) was the object of numerous studies. In modern parlance, crystal- and ligand-field theories are special cases of the theory of level splitting.

As a typical example, let us consider the case of a ruby crystal. It consists of corindon (Al_2O_3) doped with trivalent chromium ions (Cr^{3+}) in substitution with trivalent aluminum ions (Al^{3+}). The electrons of each Cr^{3+} ion are thus subjected to inhomogeneous electric fields arising from the ligands or coordinats constituted by the oxygen atoms. These electric (or crystalline) fields yield a level splitting of the energy levels of the Cr^{3+} ion. One-photon transitions in the visible between the split levels are responsible for the nice pink to blood-red color of ruby.

The distinction between crystal-field theory and ligand-field theory is as follows. In crystal-field theory one uses atomic orbitals for the central partly-filled shell ion (the Cr^{3+} ion in our example) whereas in ligand-field theory one considers molecular orbitals made of linear combinations of atomic orbitals of the central ion and of the ligands or coordinats (the O^{2-} ions in our example).

2.2 The Hamiltonian

We shall consider the common case of an ion with a ℓ^N atomic configuration (N equivalent electrons on a $n\ell$ shell outside of a set of closed shells). The $\ell = 2$ case corresponds to transition metal-ions and the $\ell = 3$ case to rare earth and actinide ions. In first approximation, the perturbation Hamiltonian $\mathcal{H}$ for such an ion embedded in a crystalline field reads

$$\mathcal{H} := \mathcal{H}_C + \mathcal{H}_{so} + \mathcal{H}_{cf} \tag{1}$$

where $\mathcal{H}_C$ stands for the two-body Coulomb interaction between the N electrons, $\mathcal{H}_{so}$ the one-body spin-orbit interaction for the N electrons and $\mathcal{H}_{cf}$ the one-body interaction between the N electrons and the environment of the central ion. Obviously, $\mathcal{H}_C$ and $\mathcal{H}_{so}$ are rotationally invariant and $\mathcal{H}_{cf}$ is invariant under the point symmetry group G of the ion and its surrounding.

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Therefore, the $O(3) \supset G$ chain of groups naturally plays an important role in the description of the ion in its environment (the three-dimensional orthogonal group $O(3)$ is isomorphic with the three-dimensional rotation group). When G contains only rotations, it is sufficient to consider the $SO(3) \supset G$ chain for N even ($SO(3)$ is the three-dimensional special orthogonal group) or the $SU(2) \supset G^*$ chain for N odd, where $SU(2)$ and G^* are the spinor groups (double groups in the terminology of Bethe) of $SO(3) \sim SU(2)/Z_2$ and $G \sim G^*/Z_2$, respectively. We can thus understand the importance of both continuous and finite groups in crystal- and ligand-field theories.

In view of the various terms in $\mathcal{H}$, we can have several families of models. The situations

$$\mathcal{H}_C > \mathcal{H}_{so} > \mathcal{H}_{cf} \tag{2}$$

and

$$\mathcal{H}_{cf} > \mathcal{H}_C > \mathcal{H}_{so} \tag{3}$$

correspond to the so-called weak-field model and the strong-field model, respectively. The strong-field model was mainly developed in the fifties by Tanabe, Sugano and Kamimura in Japan [30, 31, 32, 33, 34, 35] and by Griffith in England [36, 37, 38, 39, 40, 41, 42, 43, 44, 45], and later by Tang Au-chin and his collaborators in China [46, 47, 48, 49, 50] as well as by Smirnov and his collaborators in the former USSR [51, 52, 53, 54, 55]. The weak-field model, although worked out in the early days of crystal-field theory, was systematically developed from the sixties. In particular, a symmetry-adapted version of the weak-field model was introduced, as we mentioned in the introduction, following a suggestion of Racah by two of his students, Schoenfeld [21] and Flato [23, 24]. It was further developed by the present author and some of his collaborators [26, 27, 56, 57, 58, 59] (see also [46, 47, 48, 49, 50, 51, 52, 53, 54, 55]). In crystal-field theory, the weak- and strong-field models are *a priori* equivalent if the matrix of $\mathcal{H}$ is set up on the

$$C_{4\ell+2}^N := \frac{(4\ell + 2)!}{(4\ell + 2 - N)!N!} \tag{4}$$

state vectors of the ℓ^N configuration. Nevertheless, the implementations of the two models are quite different as it will be shown below. As an illustration, we shall now discuss in turn the two models (strong- and weak-field models) in the special case of d^N ions in cubic symmetry.

2.3 Strong-field models

It is difficult to describe the strong-field model in the general case of ℓ^N in G. Hence, we consider the case of a d^N ion ($\ell = 2$) in octahedral symmetry ($G = O$). The restriction $SO(3) \rightarrow O$ yields the following decomposition

$$2 = E \oplus T_2 \tag{5}$$

of the irreducible representation class (IRC) of $SO(3)$ associated with $\ell = 2$ into a direct sum of the IRCs E and T_2 of finite group O. As a consequence, there is a splitting level: the five

degenerate d orbitals give rise to a E doublet (with two degenerate orbitals e) and a T_2 triplet (with three degenerate orbitals t_2). The e and t_2 orbitals can be considered as symmetry-adapted atomic orbitals (in crystal-field theory) or as molecular orbitals (in ligand-field theory). The distribution of the N electrons on the t_2 and e orbitals, according to the Pauli exclusion principle, yields (molecular) configurations of type $t_2^x e^{N-x}$. Then, we can form (molecular) terms $t_2^x(S_1\Gamma_1)e^{N-x}(S_2\Gamma_2)$, where S_1 and S_2 are the total spins for the x and $N-x$ electrons on the t_2 and e orbitals, respectively. Furthermore, Γ_1 (contained in $T_2^{\otimes x}$) and Γ_2 (contained in $E^{\otimes(N-x)}$) denote the IRCs characterizing the orbital parts of the t_2 and e electrons. The next step is to couple S_1 with S_2 to get the total spin S (contained in $S_1 \otimes S_2$) and Γ_1 with Γ_2 to obtain Γ (contained in $\Gamma_1 \otimes \Gamma_2$). This leads to (molecular) states $t_2^x(S_1\Gamma_1)e^{N-x}(S_2\Gamma_2)S\Gamma$. Finally, the coupling of S (decomposed into IRCs of O^*) with Γ gives the total IRC Γ_T (an internal branching multiplicity label b is necessary when Γ_T occurs several times in the reduction of $S \otimes \Gamma$). As a result, we get state vectors of type

$$|t_2^x(S_1\Gamma_1)e^{N-x}(S_2\Gamma_2)S\Gamma b\Gamma_T\gamma_T) \tag{6}$$

which are expressed (via complicated formulas) in terms of one-electron state vectors by means of coupling coefficients and coefficients of fractional parentage. Note that the label γ_T in (6) is necessary when the dimension of Γ_T is greater than 1.

The calculation of the matrix elements of $\mathcal{H}_{cf}$ in the strong-field basis (6) is elementary. However, this is not the case for $\mathcal{H}_C + \mathcal{H}_{so}$. The construction of the matrix of $\mathcal{H}_C + \mathcal{H}_{so}$ on $C_{4\ell+2}^N$ state vectors (6) requires the knowledge of coupling and recoupling coefficients for both $SU(2)$ and G^* as well as coefficients of fractional parentage for the configurations $t_2^x e^{N-x}$.

From the practical point of view, the just described strong-field approach leads to:

- a five-parameter model in a crystal-field framework where the t_2 and e orbitals are atomic orbitals, called ordinary strong-field model, with 3 parameters for $\mathcal{H}_C$ (F_0, F_2 and F_4 of Slater or A, B and C of Racah, see the appendix), 1 parameter for $\mathcal{H}_{so}$ (ζ_{nd}) and 1 parameter for $\mathcal{H}_{cf}$ ($10Dq$)

- a fourteen-parameter model in a ligand-field framework where the t_2 and e orbitals are molecular orbitals, called generalized strong-field model, with 10 parameters for $\mathcal{H}_C$, 2 parameters for $\mathcal{H}_{so}$ and 2 parameters for $\mathcal{H}_{cf}$.

The strong-field models present several drawbacks. The case of d^N in O is difficult to extend to the case of ℓ^N in G: replacing O by G and/or d^N by ℓ^N requires that the calculation for $\mathcal{H}_C$ and $\mathcal{H}_{so}$, which involves complicated Wigner-Racah algebra developments for the G or G^* group with several phase problems, have to be done again. This kind of difficulty does not appear in a weak-field approach as shown below.

2.4 Weak-field models

In the case of ℓ^N in G, we may think to use atomic state vectors of type $|n\ell^N\alpha SLJM)$. However, such state vectors, adapted to the $SU(2) \supset U(1)$ chain, are not generally adapted to the G^* symmetry group. The idea of Racah was to use linear combinations of the vectors $|n\ell^N\alpha SLJM)$ transforming as IRCs of G^* and to employ his methods for calculating the energy matrix of $\mathcal{H}$. Therefore, the matrices for $\mathcal{H}_C$ and $\mathcal{H}_{so}$, in a $SU(2) \supset G^*$ symmetry-adapted basis, are the same as the ones of atomic spectroscopy (already calculated by Racah or easily calculable from Racah's methods) and the matrix of $\mathcal{H}_{cf}$ depends on reduced matrix elements of one-electron Racah unit tensor operators and $SU(2) \supset G^*$ symmetry-adapted Clebsch-Gordan coefficients. Thus, the implementation of the symmetry-adapted weak-field model is easier than the one of the ordinary strong-field model. Following Racah's idea, Schoenfeld and Flato calculated the matrix of $\mathcal{H}$ for the d^2 and d^3 configurations in cubic symmetry [21] and in tetragonal and trigonal symmetries [23, 24]. Later, Low and Rosengarten dealt with the case of the d^5 configuration in cubic symmetry in connection with the optical spectra of Mn_2^{2+} and Fe^{3+} ions in crystalline fields [22].

The Wigner-Racah algebra for the $SU(2)$ group in a $SU(2) \supset G^*$ symmetry-adapted basis of interest for the symmetry-adapted weak-field model was developed by the present author [26, 27, 28, 60] and further considered by several authors [61, 62, 63, 64, 65, 66, 67, 68, 69]. The main ingredients of the resulting symmetry-adapted weak-field model for ℓ^N in G can be summed up as follows.

The symmetry-adapted weak-field state vectors are of type

$$|n\ell^N\alpha SLJa\Gamma\gamma) := \sum_{M=-J}^{J} |n\ell^N\alpha SLJM)(JM|Ja\Gamma\gamma) \tag{7}$$

where Γ is an IRC of G^*, a a branching multiplicity label to be used when the (J) IRC of $SU(2)$, associated with the J quantum number, contains Γ several times and γ a multiplicity label to be used when the dimension of the Γ IRC is greater than 1. In (7), the $(JM|Ja\Gamma\gamma)$ reduction coefficients are elements of a unitary matrix which reduces the representation matrix associated with the (J) IRC of $SU(2)$ into a direct sum of representation matrices of G^*. They have to be distinguished from the reduction coefficients obtained from the diagonalization of an operator invariant under the G group [70, 71, 72, 73, 74, 75]. The $(JM|Ja\Gamma\gamma)$ reduction coefficients are chosen in such a way that the set

$$\{|n\ell^N\alpha SLJa\Gamma\gamma) : \gamma \text{ ranging}\} \tag{8}$$

spans a representation matrix associated with Γ independent of the atomic quantum numbers and that the values of the corresponding coupling coefficients (the f coefficients below) are square roots of rational numbers. Then, the matrices for $\mathcal{H}_C$ and $\mathcal{H}_{so}$ follow from

$$(n\ell^N\alpha SLJa\Gamma\gamma|\mathcal{H}_C|n\ell^N\alpha'S'L'J'a'\Gamma'\gamma') = \delta_{SS'}\delta_{LL'}\delta_{JJ'}\delta_{aa'}\delta_{\Gamma\Gamma'}\delta_{\gamma\gamma'}$$
$$\times\Delta(S,L,J)(n\ell^N\alpha SLM_SM_L|\mathcal{H}_C|n\ell^N\alpha'SLM_SM_L) \tag{9}$$

and

$$(n\ell^N\alpha SLJa\Gamma\gamma|\mathcal{H}_{so}|n\ell^N\alpha'S'L'J'a'\Gamma'\gamma') = \delta_{JJ'}\delta_{aa'}\delta_{\Gamma\Gamma'}\delta_{\gamma\gamma'}$$
$$\times (n\ell^N\alpha SLJM|\mathcal{H}_{so}|n\ell^N\alpha'S'L'JM) \tag{10}$$

where $\Delta(S,L,J)$ is 1 if S, L and J satisfy the triangular condition and 0 otherwise ; in (9) and (10), the matrix elements in the right-hand sides are independent of the magnetic quantum numbers M_S, M_L and M, respectively. Clearly, the energy matrices for $\mathcal{H}_C$ and $\mathcal{H}_{so}$ do not depend on the G group and are easily built from the works of Racah (the matrix elements in the right-hand sides of (9) and (10) are known for the p^N, d^N and f^N configurations [76] or easily calculable from computer programs). On the other hand, the matrix of $\mathcal{H}_{cf}$ can be readily set up by making use of the development

$$\mathcal{H}_{cf} = \sum_{ka_0} D[ka_0]U^{(k)}_{a_0\Gamma_0\gamma_0} \tag{11}$$

where $U^{(k)}_{a_0\Gamma_0\gamma_0}$ is a component of a Racah unit tensor operator $\mathbf{U}^k$ invariant under G (i.e., transforming as the Γ_0 identity IRC of G). In (11), $D[ka_0]$ are crystal-field parameters connected to the B^k_q parameters (in Wybourne's normalization [10, 77]) via

$$D[ka_0] = (-1)^\ell(2\ell+1)\begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}\sum_{q=-k}^{k} B^k_q(kq|ka_0\Gamma_0\gamma_0)^* \tag{12}$$

and a_0 is a branching multiplicity label to be used when Γ_0 appears several times in the decomposition of the (k) IRC of $SO(3)$. (The index γ_0 in (11) and (12) is not really necessary since Γ_0 is a one-dimensional IRC; it is mentioned only for aesthetic reasons.) Then, the matrix elements of $\mathcal{H}_{cf}$ in a $SU(2) \supset G^*$ symmetry-adapted weak-field basis are given by

$$(n\ell^N\alpha SLJa\Gamma\gamma|\mathcal{H}_{cf}|n\ell^N\alpha'S'L'J'a'\Gamma'\gamma') = \delta_{SS'}\delta_{\Gamma\Gamma'}\delta_{\gamma\gamma'}$$
$$\times \quad (-1)^{S+L'+J}\sqrt{(2J+1)(2J'+1)}\sum_{ka_0} D[ka_0] \tag{13}$$
$$\times \quad (n\ell^N\alpha SL\|U^{(k)}\|n\ell^N\alpha'SL')\begin{Bmatrix} L & k & L' \\ J' & S & J \end{Bmatrix}f\begin{pmatrix} J & J' & k \\ a\Gamma & a'\Gamma & a_0\Gamma_0 \end{pmatrix}$$

where $\{\ldots\}$ stands for a 6–j Wigner symbol and f is a coupling coefficient defined by

$$f\begin{pmatrix} J & J' & k \\ a\Gamma & a'\Gamma & a_0\Gamma_0 \end{pmatrix} \quad := \quad \sum_{M=-J}^{J}\sum_{M'=-J'}^{J'}\sum_{q=-k}^{k}(JM|Ja\Gamma\gamma)^*(kq|ka_0\Gamma_0\gamma_0)(J'M'|J'a'\Gamma\gamma)$$
$$\times \quad (-1)^{J-M}\begin{pmatrix} J & k & J' \\ -M & q & M' \end{pmatrix} \tag{14}$$

This f coefficient is independent of γ [24, 26]. It is a particular case of the f coefficient defined in [26] by

$$f\begin{pmatrix} j_1 & j_2 & k \\ \mu_1 & \mu_2 & \mu \end{pmatrix} \quad := \quad \sum_{m_1=-j_1}^{j_1}\sum_{m_2=-j_2}^{j_2}\sum_{q=-k}^{k}(j_1m_1|j_1\mu_1)^*(kq|k\mu)(j_2m_2|j_2\mu_2)$$
$$\times \quad (-1)^{j_1-m_1}\begin{pmatrix} j_1 & k & j_2 \\ -m_1 & q & m_2 \end{pmatrix} \tag{15}$$

where

$$\mu_1 := a_1\Gamma_1\gamma_1, \quad \mu_2 := a_2\Gamma_2\gamma_2, \quad \mu := a\Gamma\gamma \tag{16}$$

(see also [60]). As a conclusion, the calculation of the matrix of $\mathcal{H}$ in a symmetry-adapted weak-field basis (via (9), (10) and (13)) is considerably simpler than in a strong-field basis.

In the case of d^N in O, the just described symmetry-adapted weak-field approach, based on (9), (10) and (13), leads to a weak-field model which is equivalent to the ordinary (or ionic) strong-field model with the parameters A, B, C, ζ_{nd} and $10Dq$. More generally for ℓ^N in G, the symmetry-adapted weak-field model and the ionic strong-field model are equivalent. However for ℓ^N in G, the symmetry-adapted weak-field model and the generalized (or covalent) strong-field model are not equivalent. Thus, it is desirable to develop a generalized symmetry-adapted weak-field model equivalent to the generalized strong-field model. This will be done in the next section.

2.5 Generalized weak-field model

To generalize the symmetry-adapted weak-field model, we keep the symmetry-adapted weak-field basis (7) intact in order to take advantage of its simplicity. The sole modification to be done consists in replacing the Hamiltonian $\mathcal{H}$ by an effective Hamiltonian H_{eff}. The Hamiltonian H_{eff} for ℓ^N in G should reduce to $\mathcal{H}$ for some special values of its parameters, should be an Hermitian operator invariant under the G group and the time-reversal operator, and should contain one- and two-body spin and orbit interactions. For the sake of easy calculations, H_{eff} should involve a coupling scheme which is reminiscent of the $\{SLJ\}$ coupling scheme of the state vectors (7). Therefore, we take H_{eff} in the form

$$\begin{aligned} H_{\mathrm{eff}} \quad &:= \quad \sum_{i,j}\sum_{\text{all}\,k}\sum_{a_0} D[(k_1k_2)k_S(k_3k_4)k_Lka_0] \\ &\times \quad \{\{\mathbf{u}^{(k_1)}(i)\otimes\mathbf{u}^{(k_2)}(j)\}^{(k_S)}\otimes\{\mathbf{u}^{(k_3)}(i)\otimes\mathbf{u}^{(k_4)}(j)\}^{(k_L)}\}^{(k)}_{a_0\Gamma_0\gamma_0} \end{aligned} \tag{17}$$

where the $\mathbf{u}$'s are one-electron Racah unit tensor operators with $\{\mathbf{u}^{(k_1)}(i)\otimes\mathbf{u}^{(k_2)}(j)\}^{(k_S)}$ acting on the spin part and $\{\mathbf{u}^{(k_3)}(i)\otimes\mathbf{u}^{(k_4)}(j)\}^{(k_L)}$ on the orbital part of the state vectors (7). The sums over i and j in (17) are extended over the N electrons and the sums over the k's and a_0 are limited, like in (11), by hermiticity and symmetry properties of H_{eff} (invariance under the G group and the time-reversal operator) and by the selection rules on the matrix elements of H_{eff} in the basis (7). Furthermore, the parameters $D[(k_1k_2)k_S(k_3k_4)k_Lka_0]$ comprise the Coulomb interelectronic parameters, the spin-orbit parameters and the crystal-field parameters of the ordinary weak-field model plus some additional parameters to be described below. The most important (as far as a comparison with the generalized strong-field model is in order) parameters in H_{eff} can be classified in the following way.

1. The $D[(00)0(kk)00]$ parameters correspond to the ordinary or isotropic Coulomb interaction between the N electrons.

2. The $D[(00)0(k_3k_4)k_Lk_La_0]$ parameters with $k_L \neq 0$ correspond to anisotropic Coulomb interactions between the N electrons or ligand-field correlated Coulomb interactions.

3. The $D[(ss)1(\ell\ell)10]$ parameter corresponds to the ordinary or isotropic spin-orbit interaction for the N electrons ($s = 1/2$).

4. The $D[(ss)1(\ell\ell)k_Lka_0]$ parameters with $k_L \neq 1$ correspond to anisotropic spin-orbit interactions for the N electrons or ligand-field correlated spin-orbit interactions.

5. The $D[(ss)0(\ell\ell)k_Lk_La_0]$ parameters correspond to the ligand-field interaction.

The building of the energy matrix of H_{eff} in the basis (7) is very simple. Indeed, we have the following matrix elements

$$
\begin{aligned}
(n\ell^N\alpha SLJa\Gamma\gamma|&H_{\text{eff}}|n\ell^N\alpha'S'L'J'a'\Gamma'\gamma') = \delta_{\Gamma\Gamma'}\delta_{\gamma\gamma'} \\
\times \sum_{\text{all } k}\sum_{a_0} &D[(k_1k_2)k_S(k_3k_4)k_Lka_0]f\begin{pmatrix} J & J' & k \\ a\Gamma & a'\Gamma & a_0\Gamma_0 \end{pmatrix}\sum_{i,j} \\
\times \quad &(n\ell^N\alpha SLJ\|\{\{\mathbf{u}^{(k_1)}(i) \otimes \mathbf{u}^{(k_2)}(j)\}^{(k_S)} \otimes \{\mathbf{u}^{(k_3)}(i) \otimes \mathbf{u}^{(k_4)}(j)\}^{(k_L)}\}^{(k)}\|n\ell^N\alpha'S'L'J')
\end{aligned}
\tag{18}
$$

where the reduced matrix element ($\| \dots \|$) can be calculated from the Racah's standard methods.

The symmetry-adapted weak-field approach based on (17) and (18) leads to a model that turns out to be equivalent to the generalized strong-field model. However, the generalized symmetry-adapted weak-field model contains more parameters than the generalized strong-field model (e.g., the Hamiltonian given by (17) contains spin-spin and orbit-orbit interaction parameters that do not occur in the generalized strong-field model). The $D[(k_1k_2)k_S(k_3k_4)k_Lka_0]$ parameters can be considered as phenomenological global parameters to be fitted on experimental data. All or part of these parameters can be interpreted and calculated in the framework of *ab initio* microscopic models as for instance the angular overlap model [78, 79], the superposition model [80] and the MO-LCAO model [81, 82, 83, 84]. (See the appendix for the connection between the isotropic Coulomb interaction parameters and the Slater-Condon-Shortley parameters.) Of course, the generalized symmetry-adapted weak-field model gives back the ordinary symmetry-adapted weak-field model as a particular case when some parameters vanish.

By way of illustration, let us consider the case of d^N in O. The corresponding Hamiltonian H_{eff} can be restricted to an operator containing 14 parameters, namely,

- 10 Coulomb parameters:
  $D[(00)0(00)00]$, $D[(00)0(22)00]$, $D[(00)0(44)00]$,
  $D[(00)0(04)44]$, $D[(00)0(22)44]$, $D[(00)0(24)44]$,
  $D[(00)0(44)44]$, $D[(00)0(24)66]$, $D[(00)0(44)66]$, $D[(00)0(44)88]$;

- 2 spin-orbit parameters:
  $D[(ss)1(22)10]$, $D[(ss)1(22)34]$;

- 2 ligand-field parameters:
  $D[(ss)0(22)00]$, $D[(ss)0(22)44]$;

It can be shown that the generalized symmetry-adapted weak-field model with these 14 parameters is equivalent to the generalized strong-field model for d^N in O [58]. Such an equivalence was also worked out for the case of f^N in O. In this case, the generalized symmetry-adapted weak-field model can be restricted to involve the following 33 parameters

- 26 Coulomb parameters:
  $D[(00)0(00)00]$, $D[(00)0(22)00]$, $D[(00)0(44)00]$, $D[(00)0(66)00]$,
  $D[(00)0(04)44]$, $D[(00)0(22)44]$, $D[(00)0(24)44]$, $D[(00)0(26)44]$,
  $D[(00)0(44)44]$, $D[(00)0(46)44]$, $D[(00)0(66)44]$, $D[(00)0(06)66]$,
  $D[(00)0(24)66]$, $D[(00)0(26)66]$, $D[(00)0(44)66]$, $D[(00)0(46)66]$,
  $D[(00)0(66)66]$, $D[(00)0(26)88]$, $D[(00)0(44)88]$, $D[(00)0(46)88]$,
  $D[(00)0(66)88]$, $D[(00)0(46)99]$, $D[(00)0(46)10, 10]$, $D[(00)0(66)10, 10]$,
  $D[(00)0(66)12, 12a]$, $D[(00)0(66)12, 12b]$;

- 4 spin-orbit parameters:
  $D[(ss)1(33)10]$, $D[(ss)1(33)34]$, $D[(ss)1(33)54]$, $D[(ss)1(33)56]$;

- 3 ligand-field parameters:
  $D[(ss)0(33)00]$, $D[(ss)0(33)44]$, $D[(ss)0(33)66]$.

The generalized symmetry-adapted weak-field model with these 33 parameters is equivalent to the generalized strong-field model for f^N in O [58].

2.6 Transition intensities

In addition to be useful for the calculation of energy levels of a partly-filled shell ion in a given surrounding, the Racah's methods proved to be of considerable importance for the calculation of transitions between levels. We shall not develop these facets of crystal- and ligand-field theory here. It is enough to mention the pioneer works by Judd [85] and Ofelt [86] for one-photon electric dipolar transitions between split levels of the same parity (see also [10]). Let us also mention that the symmetry considerations developed by Bader and Gold [87] for two-photon electric dipolar transitions between states of opposite parities were reformulated in the symmetry-adapted weak-field model [59, 88, 89]. Finally, let us mention that irreducible tensor methods for finite groups were used for calculating the intensities of photoelectron spectra of partly-filled shell ion systems [90, 91, 92, 93, 94].

3 Wigner-Racah algebra for a finite or compact group

An important task in spectroscopy is to calculate matrix elements in order to determine energy spectra and transition intensities. In the case of many-fermionic systems, this can be done either in the Slater-Condon-Shortley approach (with determinantal states) or in the Dirac-Wigner-Racah approach (with states characterized by quantum numbers). In the Dirac-Wigner-Racah approach, one way to incorporate symmetry considerations connected to a chain of groups

(involving symmetry groups and classification groups) is to use the 'Wigner-Racah calculus' associated with the chain under consideration. The 'Wigner-Racah calculus' or 'Wigner-Racah algebra' associated with a group G (or a chain of groups $G_a \supset G_\Gamma$) is generally understood as the set of algebraic manipulations concerning the coupling and recoupling coefficients for the group G (or the head group G_a). This 'algebra' may be also understood as a true algebra in the mathematical sense: It is the (in)finite-dimensional Lie algebra spanned by the irreducible unit tensor operators or Wigner operators of G (or G_a) [5, 6, 9, 95, 96, 97]. We shall mainly focus here on the very basic aspects of the 'algebra' of the coupling and recoupling coefficients of a finite or compact group G. The Wigner-Racah calculus was originally developed for simply-reducible (i.e., ambivalent plus multiplicity-free) groups [98, 99, 100]. (Let us recall that a group G is said to be ambivalent if each element of G and its inverse belong to a same conjugation class. It is said to be multiplicity-free if the Kronecker product of two arbitrary irreducible representations of G contains at most once each irreducible representation of G.) The bases of the Wigner-Racah algebra of the rotation group, a simply-reducible group, were introduced at the beginning of the forties by Wigner [99] and Racah [2, 3]. In the sixties and seventies, the idea of a Wigner-Racah algebra was extended to an arbitrary finite or compact group [101, 102, 103] (see the review in [104]) and started to be applied to some groups or chains of groups of interest in crystal- and ligand-field theory [35, 45, 47, 55, 60]. Regarding molecular and solid-state physics, let us also mention that Koster *et al.* published the first complete set of tables of coupling coefficients for the thirty-two (single and double) crystallographic point groups [105]. Most of the developments concerning chains of groups were strongly influenced by a lemma due to Racah derived in [4] for an arbitrary chain involving finite and/or compact groups.

We present in what follows the basic ingredients for the Wigner-Racah algebra of a finite or compact group in a terminology easily adaptable to nuclear, atomic, molecular, and condensed matter physics as well as in quantum chemistry.

3.1   Preliminaries

Let us consider an arbitrary finite or compact continuous group G having the IRCs a, b, …. The identity IRC, often noted A or A_1 or Γ_1 in molecular physics, is denoted by 0 in this section (it is noted Γ_0 in Section 2). To each IRC a, we associate a unitary matrix representation D^a. Let $[a]$ be the dimension of D^a. The α-α' matrix element of the representative $D^a(R)$ for the element R in G is written $D^a(R)_{\alpha\alpha'}$. (For $a = 0$, we have $\alpha = \alpha' = 0$.) The sum $\chi^a(R) = \sum_\alpha D^a(R)_{\alpha\alpha}$ stands for the character of R in D^a. The $D^a(R)_{\alpha\alpha'}$ and $\chi^a(R)$ satisfy orthogonality relations (e.g., the so-called great orthogonality theorem for $D^a(R)_{\alpha\alpha'}$) that are very familiar to the physicist and the chemist. We use $|G|$ to denote the order of G when G is a finite group or the volume $\int_G dR$ of G when G is a compact continuous group. Furthermore, the notation $\int_G \ldots dR$, which applies when G is a compact continuous group, should be understood as $\sum_{R \in G} \ldots$ when G is a finite group.

3.2 Clebsch-Gordan coefficients

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

$$a \otimes b = \bigoplus_c \sigma(c|a \otimes b)c \tag{19}$$

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

$$\sigma(c|a \otimes b) = |G|^{-1} \int_G \chi^c(R)^* \chi^a(R) \chi^b(R) dR \tag{20}$$

In terms of matrix representations, (19) reads

$$D^a \otimes D^b \sim \bigoplus_c \sigma(c|a \otimes b) D^c \tag{21}$$

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

$$(U^{ab})^\dagger D^a(R) \otimes D^b(R) U^{ab} = \bigoplus_c \sigma(c|a \otimes b) D^c(R) \tag{22}$$

or equivalently

$$D^a(R) \otimes D^b(R) = \bigoplus_c \sigma(c|a \otimes b) U^{ab} D^c(R) (U^{ab})^\dagger \tag{23}$$

for any R in G. It is a simple exercise in linear algebra to transcribe (22) and (23) in matrix elements. We thus have

$$\sum_{\alpha\beta\alpha'\beta'} \left(U^{ab}\right)^*_{\alpha\beta,\rho c\gamma} D^a(R)_{\alpha\alpha'} D^b(R)_{\beta\beta'} \left(U^{ab}\right)_{\alpha'\beta',\rho' c'\gamma'} = \Delta(c|a \otimes b)\delta_{\rho\rho'}\delta_{cc'} D^c(R)_{\gamma\gamma'} \tag{24}$$

and

$$D^a(R)_{\alpha\alpha'} D^b(R)_{\beta\beta'} = \sum_{\rho c\gamma\gamma'} \left(U^{ab}\right)_{\alpha\beta,\rho c\gamma} D^c(R)_{\gamma\gamma'} \left(U^{ab}\right)^*_{\alpha'\beta',\rho c\gamma'} \tag{25}$$

for any R in G. Each row index of U^{ab} consists of two labels (α and β) according to the rules of the direct product of two matrices. Similarly, two labels (c and γ) are required for characterizing each column index of U^{ab}. 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 (25) ranges from 1 to $\sigma(c|a \otimes b)$. Finally in (24), $\Delta(c|a \otimes b) = 0$ or 1 according to whether as c is contained or not in $a \otimes b$. (Note that $\Delta(c|a \otimes b)$ is the analog of $\Delta(S, L, J)$ used in Section 2.)

Following the tradition in quantum mechanics, we put

$$(ab\alpha\beta|\rho c\gamma) := \left(U^{ab}\right)_{\alpha\beta,\rho c\gamma} \tag{26}$$

so that (24) and (25) can be rewritten as

$$\sum_{\alpha\beta\alpha'\beta'} (ab\alpha\beta|\rho c\gamma)^* D^a(R)_{\alpha\alpha'} D^b(R)_{\beta\beta'} (ab\alpha'\beta'|\rho'c'\gamma') = \Delta(c|a \otimes b)\delta_{\rho\rho'}\delta_{cc'} D^c(R)_{\gamma\gamma'} \tag{27}$$

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and

$$D^a(R)_{\alpha\alpha'}D^b(R)_{\beta\beta'} = \sum_{\rho c \gamma\gamma'}(ab\alpha\beta|\rho c\gamma)D^c(R)_{\gamma\gamma'}(ab\alpha'\beta'|\rho c\gamma')^* \tag{28}$$

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

$$\sum_{\alpha\beta}(ab\alpha\beta|\rho c\gamma)^*(ab\alpha\beta|\rho' c'\gamma') = \Delta(c|a\otimes b)\delta_{\rho\rho'}\delta_{cc'}\delta_{\gamma\gamma'} \tag{29}$$

and

$$\sum_{\rho c\gamma}(ab\alpha\beta|\rho c\gamma)(ab\alpha'\beta'|\rho c\gamma)^* = \delta_{\alpha\alpha'}\delta_{\beta\beta'} \tag{30}$$

Note that (29) and (30) are conveniently recovered by specializing R to the unit element E of G in (27) and (28), respectively. As an evident selection rule on the CCGs, it is clear that in order to have $(ab\alpha\beta|\rho c\gamma) \neq 0$ it is necessary (but not sufficient) that c be contained in $a\otimes b$.

Equations (27) and (28) show that the CGCs are basis-dependent coefficients. In this regard, it is important to realize that (27) and (28) are not sufficient to define unambiguously the CGCs of the G group once its irreducible representation matrices are known. As a matter of fact, the relation

$$(ab\alpha\beta|rc\gamma) := \sum_{\rho}(ab\alpha\beta|\rho c\gamma)M(ab,c)_{\rho r} \tag{31}$$

where $M(ab,c)$ is an arbitrary unitary matrix of dimension $\sigma(c|a\otimes b)\times\sigma(c|a\otimes b)$, defines a new set of CGCs since (27) and (28) are satisfied by making replacements of type $\rho \to r$. The CGCs associated with 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 symmetry properties of the CGCs.

Various relations involving elements of irreducible representation matrices and CGCs can be derived from (27) and (28) by using the unitarity property both for the representation matrices and the Clebsch-Gordan matrices. For instance, we obtain

$$\sum_{\alpha'\beta'}D^a(R)_{\alpha\alpha'}D^b(R)_{\beta\beta'}(ab\alpha'\beta'|\rho c\gamma') = \sum_{\gamma}(ab\alpha\beta|\rho c\gamma)D^c(R)_{\gamma\gamma'} \tag{32}$$

$$\sum_{\alpha'}D^a(R)_{\alpha\alpha'}(ab\alpha'\beta'|\rho c\gamma') = \sum_{\beta\gamma}(ab\alpha\beta|\rho c\gamma)D^b(R)^*_{\beta\beta'}D^c(R)_{\gamma\gamma'} \tag{33}$$

$$(ab\alpha'\beta'|\rho c\gamma') = \sum_{\alpha\beta\gamma}(ab\alpha\beta|\rho c\gamma)D^a(R)^*_{\alpha\alpha'}D^b(R)^*_{\beta\beta'}D^c(R)_{\gamma\gamma'} \tag{34}$$

for any R in G. In the situation where the elements of the irreducible representation matrices of G are known, Eqs. (32), (33) and (34) provide us with linear equations useful for checking the numerical values of the CGCs of G.

The combination of (28) with the great orthogonality theorem for G yields the relation

$$|G|^{-1} \int_G D^a(R)_{\alpha\alpha'} D^b(R)_{\beta\beta'} D^c(R)^*_{\gamma\gamma'} dR = [c]^{-1} \sum_\rho (ab\alpha\beta|\rho c\gamma)(ab\alpha'\beta'|\rho c\gamma')^* \tag{35}$$

which is useful for the calculation of the CGCs 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 (35)), Eq. (35) allows us to determine $(ab\alpha\beta|c\gamma)$ for all α, β and γ up to arbitrary phase factors ; more precisely, we then have

$$(ab\alpha\beta|c\gamma) = e^{ih(ab,c)} \left(\frac{[c]}{|G|} \right)^{1/2} \frac{\int_G D^a(R)_{\alpha\alpha'} D^b(R)_{\beta\beta'} D^c(R)^*_{\gamma\gamma'} dR}{\{\int_G D^a(R)_{\alpha'\alpha'} D^b(R)_{\beta'\beta'} D^c(R)^*_{\gamma'\gamma'} dR\}^{1/2}} \tag{36}$$

where $h(ab, c) \in \mathbb{R}$.

It appears from (32)-(36) that c does not generally play the same role as a and b in $(ab\alpha\beta|\rho c\gamma)$. Indeed, (34) shows that the CGCs $(ab\alpha\beta|\rho c\gamma)$ are the components of a third rank tensor, twice contravariant and once covariant. Therefore, $(ab\alpha\beta|\rho c\gamma)$ does not generally exhibit simple symmetry properties under permutations of a, b and c. It will be shown in the following how the CGCs may be symmetrized thanks to a 2–$a\alpha$ symbol.

3.3   The 2–$a\alpha$ symbol

Let us define the 2–$a\alpha$ symbol through

$$\begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix} := [a]^{1/2}(ba\beta\alpha|00) \tag{37}$$

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

$$\sum_{\alpha\alpha'} \begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix}^* D^a(R)_{\alpha\alpha'} \begin{pmatrix} a & b' \\ \alpha' & \beta' \end{pmatrix} = \Delta(0|a \otimes b)\delta_{bb'} D^b(R)^*_{\beta\beta'} \tag{38}$$

and

$$\sum_{\beta\beta'} \begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix} D^b(R)^*_{\beta\beta'} \begin{pmatrix} a' & b \\ \alpha' & \beta' \end{pmatrix}^* = \Delta(0|a \otimes b)\delta_{aa'} D^a(R)_{\alpha\alpha'} \tag{39}$$

that hold for any R in G. The proof of (38) and (39) is long; it starts with the introduction of (37) into the left-hand sides of (38) and (39) and requires repeated use of relations involving the irreducible matrix representations and CGCs as well as the great orthogonality theorem of G. By taking $R = E$ in (38) and (39), we get the useful relations

$$\sum_\alpha \begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix}^* \begin{pmatrix} a & b' \\ \alpha & \beta' \end{pmatrix} = \Delta(0|a \otimes b)\delta_{bb'}\delta_{\beta\beta'} \tag{40}$$

and

$$\sum_{\beta} \begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix} \begin{pmatrix} a' & b \\ \alpha' & \beta \end{pmatrix}^* = \Delta(0|a \otimes b)\delta_{aa'}\delta_{\alpha\alpha'} \tag{41}$$

which give back (29) as particular case.

The 2–$a\alpha$ symbol turns out to be of relevance for handling phase problems. In this regard, both (38) and (39) lead to

$$\delta_{ab}\sum_{\alpha\beta} \begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix}^* \begin{pmatrix} b & a \\ \beta & \alpha \end{pmatrix} = \Delta(0|a \otimes b)[a]c_a \tag{42}$$

where the Frobenius-Schur coefficient

$$c_a := |G|^{-1}\int_G \chi^a(R^2)dR \tag{43}$$

is 1, -1, or 0 according to as D^a is orthogonal, symplectic, or complex (i.e., integer, half-integer or complex in Wigner's terminology). Note that

$$c_a \begin{pmatrix} b & a \\ \beta & \alpha \end{pmatrix} = \delta_{ab} \begin{pmatrix} a & b \\ \alpha & \beta \end{pmatrix} \tag{44}$$

satisfies (42). Equation (44) reflects the symmetry of the matrix which enables to pass from the matrix D^a to its complex conjugate $(D^a)^*$ (cf., the Frobenius-Schur theorem). Thus, the 2–$a\alpha$ symbol plays the role of a metric tensor that transforms D^a into $(D^a)^*$. It generalizes the Herring-Wigner metric tensor introduced for the $SU(2)$ group (see [99]).

3.4   The $(3\text{–}a\alpha)_\rho$ symbol

We now define the $(3\text{–}a\alpha)_\rho$ symbol via

$$\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_\rho := \sum_{\rho'c'\gamma'}[c']^{-1/2}M(ba,c')_{\rho'\rho}\begin{pmatrix} c & c' \\ \gamma & \gamma' \end{pmatrix}(ba\beta\alpha|\rho'c'\gamma') \tag{45}$$

where $M(ba,c')$ is an arbitrary unitary matrix. Conversely, each CGC can be developed in terms of $(3\text{–}a\alpha)_\rho$ symbols since the inversion of (45) gives

$$(ab\alpha\beta|\rho c\gamma) = [c]^{1/2}\sum_{\rho'c'\gamma'}M(ab,c)_{\rho\rho'}^*\begin{pmatrix} c' & c \\ \gamma' & \gamma \end{pmatrix}^*\begin{pmatrix} b & a & c' \\ \beta & \alpha & \gamma' \end{pmatrix}_{\rho'} \tag{46}$$

after utilization of the unitarity property of the 2–$a\alpha$ symbol and of the matrix $M(ba,c')$.

All the relations involving CGCs may be transcribed in terms of $(3\text{–}a\alpha)_\rho$ symbols. For example, the orthonormality relations (29) and (30) are easily amenable to the form

$$\sum_{\rho c\gamma}[c]\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_\rho\begin{pmatrix} a & b & c \\ \alpha' & \beta' & \gamma \end{pmatrix}_\rho^* = \delta_{\alpha\alpha'}\delta_{\beta\beta'} \tag{47}$$

and

$$\sum_{\alpha\beta}\begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_\rho^*\begin{pmatrix} a & b & c' \\ \alpha & \beta & \gamma' \end{pmatrix}_{\rho'} = \Delta(0|a \otimes b \otimes c)\delta_{\rho\rho'}\delta_{cc'}\delta_{\gamma\gamma'}[c]^{-1} \tag{48}$$

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Along the same line, the introduction of (46) into (28) yields

$$D^a(R)_{\alpha\alpha'} D^b(R)_{\beta\beta'} = \sum_{\rho c \gamma \gamma'} [c] \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_\rho D^c(R)^*_{\gamma\gamma'} \begin{pmatrix} a & b & c \\ \alpha' & \beta' & \gamma' \end{pmatrix}^*_\rho \tag{49}$$

which in turn leads to

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

$$= \Delta(0|a \otimes b \otimes c) \delta_{\rho\rho'} \delta_{cc'} [c]^{-1} D^c(R)^*_{\gamma\gamma'} \tag{50}$$

owing to the orthogonality relation (48). Equations (49) and (50) hold for any element R in G. As a check, note that for $R = E$, they can be specialized to (47) and (48).

Relation (49) and its dual relation (50) show that D^a, D^b and D^c present the same variance. This can be made precise by

$$\begin{pmatrix} a & b & c \\ \alpha' & \beta' & \gamma' \end{pmatrix}_\rho = \sum_{\alpha\beta\gamma} \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_\rho D^a(R)^*_{\alpha\alpha'} D^b(R)^*_{\beta\beta'} D^c(R)^*_{\gamma\gamma'} \tag{51}$$

which shows that the behavior of the $(3-a\alpha)_\rho$ symbol under permutations 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 following relation (to be compared to (35))

$$|G|^{-1} \int_G D^a(R)_{\alpha\alpha'} D^b(R)_{\beta\beta'} D^c(R)_{\gamma\gamma'} dR = \sum_\rho \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix}_\rho \begin{pmatrix} a & b & c \\ \alpha' & \beta' & \gamma' \end{pmatrix}^*_\rho \tag{52}$$

which may be proved directly by combining (49) with the great orthogonality theorem for the G group. When the triple direct product $a \otimes b \otimes c$ contains the identity IRC of G only once (i.e., when there is no label ρ and no summation in (52)), Eq. (52) shows that the square modulus of the $3-a\alpha$ symbol is invariant under permutation of its columns. In this case, we may take advantage of the arbitrariness of the matrix M in (31) or (45) to produce convenient symmetry properties of the $3-a\alpha$ symbol under permutations of its columns. By way of illustration, let us mention the following result [99]: For G simply reducible, it is possible to arrange that the numerical value of the $3-a\alpha$ symbol 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 the $3-a\alpha$ symbol remains unchanged under an even permutation of its columns (since $c_a c_b c_c = 1$).

To close this subsection, we note that the $(3-a\alpha)_\rho$ symbol constitutes a generalization to the case of an arbitrary finite or compact group of the $3-jm$ symbol introduced by Wigner for simply reducible groups (in particular for the rotation group) [99] and of the $\overline{V}$ symbol introduced by Fano and Racah for the $SU(2)$ group [7] (the $\overline{V}$ symbol is a symmetrized version of the V symbol defined by Racah [2]).

3.5 Recoupling coefficients

We now define two new coefficients:

$$(a(bc)\rho_{bc} c_{bc} \rho' d' \delta' | (ab) \rho_{ab} c_{ab} c \rho d \delta) := \sum_{\alpha\beta\gamma} \sum_{\gamma_{ab}\gamma_{bc}} (ab\alpha\beta|\rho_{ab} c_{ab} \gamma_{ab})(c_{ab} c \gamma_{ab} \gamma | \rho d \delta)$$

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$$\times \quad (bc\beta\gamma|\rho_{bc}c_{bc}\gamma_{bc})^*(ac_{bc}\alpha\gamma_{bc}|\rho'd'\delta')^* \tag{53}$$

and

$$((ac)\rho_{ac}c_{ac}(bd)\rho_{bd}c_{bd}\rho'e'\varepsilon'|(ab)\rho_{ab}c_{ab}(cd)\rho_{cd}c_{cd}\rho e\varepsilon)$$
$$:= \sum_{\alpha\beta\gamma\delta}\sum_{\gamma_{ab}\gamma_{cd}}\sum_{\gamma_{ac}\gamma_{bd}}(ab\alpha\beta|\rho_{ab}c_{ab}\gamma_{ab})(cd\gamma\delta|\rho_{cd}c_{cd}\gamma_{cd})(c_{ab}c_{cd}\gamma_{ab}\gamma_{cd}|\rho e\varepsilon) \tag{54}$$
$$\times \quad (ac\alpha\gamma|\rho_{ac}c_{ac}\gamma_{ac})^*(bd\beta\delta|\rho_{bd}c_{bd}\gamma_{bd})^*(c_{ac}c_{bd}\gamma_{ac}\gamma_{bd}|\rho'e'\varepsilon')^*$$

The introduction in these definitions of (34) and the use of the great orthogonality theorem for G leads to the properties

$$(a(bc)\rho_{bc}c_{bc}\rho'd'\delta'|(ab)\rho_{ab}c_{ab}c\rho d\delta)$$
$$= \delta_{dd'}\delta_{\delta\delta'}[d]^{-1}\sum_{\delta}(a(bc)\rho_{bc}c_{bc}\rho'd\delta|(ab)\rho_{ab}c_{ab}c\rho d\delta) \tag{55}$$

and

$$((ac)\rho_{ac}c_{ac}(bd)\rho_{bd}c_{bd}\rho'e'\varepsilon'|(ab)\rho_{ab}c_{ab}(cd)\rho_{cd}c_{cd}\rho e\varepsilon)$$
$$= \delta_{ee'}\delta_{\varepsilon\varepsilon'}[e]^{-1}\sum_{\varepsilon}((ac)\rho_{ac}c_{ac}(bd)\rho_{bd}c_{bd}\rho'e\varepsilon|(ab)\rho_{ab}c_{ab}(cd)\rho_{cd}c_{cd}\rho e\varepsilon) \tag{56}$$

so that the recoupling coefficients defined by (53) and (54) are basis-independent (i.e., they do not depend on the labels of type α) in contrast with the coupling coefficients $(ab\alpha\beta|\rho c\gamma)$.

By using the orthonormality of the CGCs, it can be shown that the CCGs occurring in Eqs. (53) and (54) can be moved from the right hand side to the left hand side in such a way to produce new relations for which the total number of CGCs remains equal to 4 and 6, respectively. Repeated actions of this type lead to orthonormality relations for the recoupling coefficients (53) and (54).

In a way paralleling the passage from the coupling coefficients to the $(3\text{–}a\alpha)_\rho$ symbol, one can define $(6\text{–}a)_{4\rho}$ and $(9\text{–}a)_{6\rho}$ symbols from the recoupling coefficients defined by (53)-(56). The defining expressions $(6\text{–}a)_{4\rho}$ 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 as well as the defining expressions for higher $(3N\text{–}a)_{2N\rho}$ symbols corresponding to the recoupling of $N \geq 4$ IRCs. Finally, note that the recoupling coefficients and their associated $(3N\text{–}a)_{2N\rho}$ symbols, $N > 1$, for a G group can be connected to other basis-independent quantities, viz., the characters of G [101, 106].

3.6 Irreducible tensorial sets

Let $\{|\tau a\alpha) : \alpha = 1, 2, \ldots, [a]\}$ be a basis for the irreducible matrix representation D^a of G. The vectors $|\tau a\alpha)$ are defined on a unitary or pre-Hilbert space $\mathcal{E}$ (indeed, a Hilbert space in the quantum-mechanical applications) and there exists an application $R \mapsto P_R$ such that

$$P_R|\tau a\alpha) = \sum_{\alpha'=1}^{[a]}|\tau a\alpha')D^a(R)_{\alpha'\alpha} \tag{57}$$

for any R in G. Following the work by Fano and Racah [7] on the $SU(2)$ group, we refer the set $\{|\tau a\alpha) : \alpha = 1, 2, \ldots, [a]\}$ to as an irreducible tensorial set (ITS) of vectors associated with D^a. The label τ may serve to distinguish different ITSs of vectors associated with the same irreducible matrix representation D^a. (In practical applications, this label consists of various quantum numbers arising from nuclear, atomic or molecular configurations.) In this connection, note the following standardization: It is always possible to arrange that $\{|\tau a\alpha) : \alpha = 1, 2, \ldots, [a]\}$ and $\{|\tau' a\alpha) : \alpha = 1, 2, \ldots, [a]\}$ span the same matrix representation D^a rather than two equivalent representations. We shall assume that such a standardization is always satisfied.

From two ITSs $\{|\tau_a a\alpha) : \alpha = 1, 2, \ldots, [a]\}$ and $\{|\tau_b b\beta) : \beta = 1, 2, \ldots, [b]\}$, we can construct another ITS of vectors. Let us define

$$|\tau_a \tau_b ab\rho c\gamma) := \sum_{\alpha\beta} |\tau_a a\alpha) \otimes |\tau_b b\beta)(ab\alpha\beta|\rho c\gamma) \tag{58}$$

Then, as a simple corollary of (28), the set $\{|\tau_a \tau_b ab\rho c\gamma) : \gamma = 1, 2, \ldots, [c]\}$ can be shown to be an ITS associated with D^c.

In a similar way, let us consider a set $\{T^a_\alpha : \alpha = 1, 2, \ldots, [a]\}$ of (linear) operators defined on $\mathcal{E}$ and such that

$$P_R T^a_\alpha P_R^{-1} = \sum_{\alpha'=1}^{[a]} T^a_{\alpha'} D^a(R)_{\alpha'\alpha} \tag{59}$$

for any R in G. This set is called an ITS of operators associated with D^a. We also say that this set defines an irreducible tensor operator $\mathbf{T}^a$ associated with D^a. Note the implicit standardization: The sets $\{T^a_\alpha : \alpha = 1, 2, \ldots, [a]\}$ and $\{U^a_\alpha : \alpha = 1, 2, \ldots, [a]\}$ span the same matrix representation D^a rather than two equivalent representations.

In full analogy with (58), we define

$$\{\mathbf{T}^a \otimes \mathbf{U}^b\}^{\rho c}_\gamma := \sum_{\alpha\beta} T^a_\alpha U^b_\beta (ab\alpha\beta|\rho c\gamma) \tag{60}$$

from the two ITSs $\{T^a_\alpha : \alpha = 1, 2, \ldots, [a]\}$ and $\{U^b_\alpha : \beta = 1, 2, \ldots, [b]\}$. As a result, the set $\{\{\mathbf{T}^a \otimes \mathbf{U}^b\}^{\rho c}_\gamma : \gamma = 1, 2, \ldots, [c]\}$ is an ITS of operators associated with 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 (60) gives the various irreducible components of $\{\mathbf{T}^a \otimes \mathbf{U}^b\}$.

3.7 The 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 $T^b_\beta|\tau a\alpha)$ vector by the $|\tau' a'\alpha')$ vector. By developing the identity

$$(\tau' a'\alpha'|T^b_\beta|\tau a\alpha) = (\tau' a'\alpha'|P_R^\dagger P_R T^b_\beta P_R^{-1} P_R|\tau a\alpha) \tag{61}$$

we get, after some manipulations, the following basic theorem.

Theorem 1 (Wigner-Eckart's theorem). The scalar product $(\tau'a'\alpha'|T_\beta^b|\tau a\alpha)$ can be decomposed as

$$(\tau'a'\alpha'|T_\beta^b|\tau a\alpha) = \sum_\rho (\tau'a'||T^b||\tau a)_\rho \sum_{a''\alpha''} \begin{pmatrix} a'' & a' \\ \alpha'' & \alpha' \end{pmatrix} \begin{pmatrix} b & a & a'' \\ \beta & \alpha & \alpha'' \end{pmatrix}_\rho^* \tag{62}$$

Alternatively, (62) can be cast into the form

$$(\tau'a'\alpha'|T_\beta^b|\tau a\alpha) = [a']^{-\frac{1}{2}} \sum_\rho \langle\tau'a'||T^b||\tau a\rangle_\rho (ab\alpha\beta|\rho a'\alpha')^* \tag{63}$$

with

$$\langle\tau'a'||T^b||\tau a\rangle_\rho := \sum_{\rho'} M(ab,a')_{\rho\rho'}^* (\tau'a'||T^b||\tau a)_{\rho'} \tag{64}$$

where $M(ab,a')$ is an arbitrary unitary matrix (cf., (45) and (46)).

In the summation-factorization afforded by (62) or (63), there are two types of terms, namely, the $(3-a\alpha)_\rho$ symbols or the CGCs $(ab\alpha\beta|\rho a'\alpha')$ that depend on the G group only and the so-called reduced matrix elements $(\tau'a'||T^b||\tau a)_\rho$ or $\langle\tau'a'||T^b||\tau a\rangle_\rho$ that depend both on G and on the physics of the problem under consideration. The reduced matrix elements do not depend on the 'magnetic quantum numbers' (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 $(\tau'_a\tau'_b a'b'\rho'c'\gamma'|\{\mathbf{T}^d \otimes \mathbf{U}^e\}_\varphi^{\sigma f}|\tau_a\tau_b ab\rho c\gamma)$ can be expressed in terms of the recoupling coefficients defined by (54) and (56).

Equations (62) and (63) generalize the Wigner-Eckart theorem originally derived by Eckart for vector operators of the rotation group [107], by Wigner for tensor operators of the rotation group [108] and of simply reducible groups [99], and by Racah for tensor operators of the rotation group [2].

A useful selection rule on the matrix element $(\tau'a'\alpha'|T_\beta^b|\tau a\alpha)$ immediately follows from the CGCs in (63). The latter matrix element vanishes if the direct product $a \otimes b$ does not contains a'. Consequently, in order to have $(\tau'a'\alpha'|T_\beta^b|\tau a\alpha) \neq 0$, it is necessary (but not sufficient in general) that the IRC a' be contained in $a \otimes b$.

As an interesting particular case, let us consider the situation where b is the identity IRC of G. This means that the operator $H = T_0^0$ is invariant under G (see (59)). Equation (63) can be particularized to

$$(\tau'a'\alpha'|H|\tau a\alpha) = \delta_{aa'}\delta_{\alpha\alpha'}\langle\tau'a||T^0||\tau a\rangle \tag{65}$$

where the index ρ is not necessary since $a \otimes 0 = a$. The Kronecker deltas in (65) show that there are no a'-a and/or α'-α mixing. We say that a and α are 'good quantum numbers' for H. The

initial and final states have the same quantum numbers as far as these numbers are associated with the invariance group G. The invariant H does not mix state vectors belonging to different irreducible representations a and a'. Furthermore, it does not mix state vectors belonging to the same irreducible representation a but having different labels α and α'.

It is very important to realize that phase factors of type $(-1)^a$, $(-1)^{a-\alpha}$ and $(-1)^{a+b+c}$ do not appear in (62) and (63). Indeed, the present exposure is entirely free of such phase factors, in contrast with other presentations. As a matter of fact, in many works the passage from the Clebsh-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 (45) and (46). Such a fact does not mean that (45) and (46) as well as other general relations are free of arbitrary phase factors. In fact, all the phase factors are implicitly contained in the matrices M, the $2\text{--}a\alpha$ symbols and the (basis-independent) Frobenius-Schur coefficient.

3.8   The Racah lemma

We have already emphasized the interest of considering chains of groups rather than isolated groups. Let us now denote G as G_a and let G_Γ be a subgroup of G_a. In this case, the labels of type α, that occur in what precedes, may be replaced by triplets of type $\alpha\Gamma\gamma$. The label of type Γ stands for an IRC of the group G_Γ, the label of type γ is absolutely necessary when $[\Gamma] > 1$ and the new label of type α is a branching multiplicity label to be used when the Γ IRC of G_Γ is contained several times in the a IRC of the G_a head group. (The γ label is an internal multiplicity label for G_Γ and the a label is an external multiplicity label inherent to the restriction $G_a \to G_\Gamma$.) Then, the $(a_1 a_2 \alpha_1 \alpha_2 | \rho a \alpha)$ CGC for the G_a group is replaced by the $(a_1 a_2 \alpha_1 \Gamma_1 \gamma_1 \alpha_2 \Gamma_2 \gamma_2 | \rho a \alpha \Gamma \gamma)$ CGC for the G_a group in a $G_a \supset G_\Gamma$ basis. We can prove the following theorem.

Theorem 2 (Racah's lemma). The CGCs of the G_a group in a $G_a \supset G_\Gamma$ basis can be developed according to

$$(a_1 a_2 \alpha_1 \Gamma_1 \gamma_1 \alpha_2 \Gamma_2 \gamma_2 | \rho a \alpha \Gamma \gamma) = \sum_\beta (\Gamma_1 \Gamma_2 \gamma_1 \gamma_2 | \beta \Gamma \gamma)(a_1 \alpha_1 \Gamma_1 + a_2 \alpha_2 \Gamma_2 | \rho a \alpha \Gamma)_\beta \qquad (66)$$

where the $(\Gamma_1 \Gamma_2 \gamma_1 \gamma_2 | \beta \Gamma \gamma)$ coefficients are CGCs for the G_Γ group considered as an isolated group and the $(a_1 \alpha_1 \Gamma_1 + a_2 \alpha_2 \Gamma_2 | \rho a \alpha \Gamma)_\beta$ coefficients do not depend on γ_1, γ_2 and γ.

The proof of Racah's lemma was originally obtained from Schur's lemma [4]. However, the analogy between (62), (63) and (66) should be noted. Hence, the Racah lemma for a $G_a \supset G_\Gamma$ chain may be derived from the Wigner-Eckart theorem, for the G_a group in a $G_a \supset G_\Gamma$ basis, applied to the Wigner operator, i.e., the operator whose matrix elements are the CGCs. The $(a_1 \alpha_1 \Gamma_1 + a_2 \alpha_2 \Gamma_2 | \rho a \alpha \Gamma)_\beta$ in the development given by (66) are sometimes named isoscalar factors, a terminology that comes from the $SU(3) \supset U(1) \otimes SU(2)$ chain used in the eightfold way model of subatomic physics.

From a purely group-theoretical point of view, it is worth to note that Racah's lemma enables

us to calculate the CGCs of the G_Γ subgroup of G_a when those of the G_a group are known (see for example [109] and references therein). In particular, for those triplets $(\Gamma_1 \Gamma_2 \Gamma)$ for which $\Gamma_1 \otimes \Gamma_2$ contains Γ only once, the CGCs $(\Gamma_1 \Gamma_2 \gamma_1 \gamma_2 | \Gamma \gamma)$ are given by a simple formula in terms of the CGCs of G_a.

The summation-factorization in (66) can be applied to each CGC entering the definition of any recoupling coefficient for the G_a group. Therefore, the recoupling coefficients for G_a can be developed in terms of the recoupling coefficients for its subgroup G_Γ [28, 60].

3.9   Illustrative examples

3.9.1   THE $SU(2)$ GROUP IN A $SU(2) \supset U(1)$ BASIS

As a first example, we take $G_a \equiv SU(2)$ and $G_\Gamma \equiv U(1)$ where $SU(2$ and $U(1)$ are the universal covering groups or, in the terminology of molecular physics, the 'double' groups of the proper rotation groups $R(3) \sim SO(3)$ and $R(2) \sim SO(2)$, respectively. In this case, $a \equiv (j)$ where j is either an integer (for vector representations) or a half-of-an-odd integer (for spinor representations), $\alpha\Gamma\gamma \equiv m$ ranges from $-j$ to j by unit step, and $D^a(R)_{\alpha\alpha'}$ can be identified to the element $D^{(j)}(R)_{mm'}$ of the well-known Wigner rotation matrix of dimension $[j] \equiv 2j + 1$. The matrix representation $D^{(j)}$ corresponds to the standard basis $\{|j, m) : m = j, j - 1, \ldots, -j\}$ where $|j, m)$ denotes an eigenvector of the (generalized) 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 IRCs of the rotation group $C_\infty \sim R(2)$. Therefore, the basis $\{|j, m) : m = j, j - 1, \ldots, -j\}$ is called a $R(3) \supset R(2)$ or $SU(2) \supset U(1)$ basis. Furthermore, the multiplicity label ρ is not necessary since $SU(2)$ is multiplicity-free. Consequently, the (real) CGCs of $SU(2)$ in a $SU(2) \supset U(1)$ basis are written $(j_1 j_2 m_1 m_2 | j m)$. They are also called Wigner coefficients.

In view of the ambivalent nature of $SU(2)$, the 2–$a\alpha$ symbol reduces here to

$$\begin{pmatrix} j & j' \\ m & m' \end{pmatrix} = \delta_{jj'} \begin{pmatrix} j \\ m & m' \end{pmatrix} \tag{67}$$

We can take

$$\begin{pmatrix} j \\ m & m' \end{pmatrix} := (-1)^{j+m} \delta(m', -m) \tag{68}$$

where $(-1)^{j+m} \delta(m', -m)$ is a component of the $1-jm$ Herring-Wigner metric tensor (in the Edmonds normalization [110]). Then, the introduction of (67) and (68) into (45) for the $SU(2) \supset U(1)$ chain shows that the 3–$a\alpha$ symbol identifies to the 3–jm Wigner symbol

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} := (2j_3 + 1)^{-\frac{1}{2}} (-1)^{j_3 - m_3 - 2j_2} (j_2 j_1 m_2 m_1 | j_3, -m_3) \tag{69}$$

provided we chose $M(j_2 j_1, j_3) = (-1)^{2j_1}$. Such a choice ensures that the 3–jm symbol is highly symmetrical under permutation of its columns.

In the $SU(2)$ case, the $(6\text{–}a)_{4\rho}$ and $(9\text{–}a)_{6\rho}$ symbols may be chosen to coincide with the $6\text{–}j$ Wigner (or $\bar{W}$ Fano-Racah) symbol and the $9\text{–}j$ Wigner (or X Fano-Racah) symbol, respectively. More precisely, we have

$$
\begin{Bmatrix} j_1 & j_{23} & j \\ j_3 & j_{12} & j_2 \end{Bmatrix} := (-1)^{j_1+j_2+j_3+j}[(2j_{12}+1)(2j_{23}+1)]^{-\frac{1}{2}}
$$
$$
\times \quad (j_1(j_2j_3)j_{23}jm|(j_1j_2)j_{12}j_3jm) \tag{70}
$$

and

$$
\begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{Bmatrix} := [(2j_{12}+1)(2j_{34}+1)(2j_{13}+1)(2j_{24}+1)]^{-\frac{1}{2}}
$$
$$
\times \quad ((j_1j_3)j_{13}(j_2j_4)j_{24}jm|(j_1j_2)j_{12}(j_3j_4)j_{34}jm) \tag{71}
$$

in terms of recoupling coefficients (cf., (55) and (56)).

Finally, for $a \equiv (k)$, the $\mathbf{T}^a$ ITS coincides with the $\mathbf{T}^{(k)}$ irreducible tensor operator of rank k (and having $2k+1$ components) introduced by Racah. We denote by $T_q^{(k)}$ the components of $\mathbf{T}^{(k)}$ in a $SU(2) \supset U(1)$ basis.

All the relations of subsections 3.1-3.7 may be rewritten as familiar relations of angular momentum theory owing to the just described correspondence rules. For example, (38) or (39) and (62) can be specialized to

$$
D^{(j)}(R)^*_{mm'} = (-1)^{m-m'} D^{(j)}(R)_{-m,-m'} \tag{72}
$$

and

$$
(\tau'j'm'|T_q^{(k)}|\tau jm) = (-1)^{j'-m'} \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix} (\tau'j'||T^{(k)}||\tau j) \tag{73}
$$

respectively. For more details, the reader should consult the textbooks in Refs. [7, 110] (see also [9, 10, 11]).

3.9.2 The $SU(2)$ group in a $SU(2) \supset G^*$ basis

We now consider the case $G_a \equiv SU(2)$ and $G_\Gamma \equiv G^*$, where G^* is isomorphic to the double group of a point (proper) rotation group G. Then, we have $a \equiv (j)$ and we take $\alpha\Gamma\gamma \equiv a\Gamma\gamma$ for the labels a and $\alpha\Gamma\gamma$ of Section 3.8. This will be clarified below.

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^*:

$$
(j) = \sum_\Gamma \sigma(\Gamma|j)\Gamma \tag{74}
$$

where

$$
\sigma(\Gamma|j) = |G^*|^{-1} \int_{G^*} dR\chi^\Gamma(R)^*\chi^{(j)}(R) \tag{75}
$$

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

$$D^{(j)} \sim \bigoplus_{\Gamma} \sigma(\Gamma|j)D^{\Gamma} \tag{76}$$

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

$$(U^j)^{\dagger}D^{(j)}(R)U^j = \bigoplus_{\Gamma} \sigma(\Gamma|j)D^{\Gamma}(R) \tag{77}$$

holds for any R in G^*. This leads to

$$\sum_{mm'}(jm|ja\Gamma\gamma)^*D^{(j)}(R)_{mm'}(jm'|ja'\Gamma'\gamma') = \delta_{aa'}\delta_{\Gamma\Gamma'}D^{\Gamma}(R)_{\gamma\gamma'} \tag{78}$$

or

$$D^{(j)}(R)_{mm'} = \sum_{a\Gamma\gamma\gamma'}(jm|ja\Gamma\gamma)D^{\Gamma}(R)_{\gamma\gamma'}(jm'|ja\Gamma\gamma')^* \tag{79}$$

for any R in G^*. In (78) and (79), $(jm|ja\Gamma\gamma)$ denotes an element of the matrix U^j:

$$(jm|ja\Gamma\gamma) := (U^j)_{m,a\Gamma\gamma} \tag{80}$$

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 (78) and (79):

$$\sum_{m}(jm|ja\Gamma\gamma)^*(jm|ja'\Gamma'\gamma') = \delta_{aa'}\delta_{\Gamma\Gamma'}\delta_{\gamma\gamma'} \tag{81}$$

or inversely

$$\sum_{a\Gamma\gamma}(jm|ja\Gamma\gamma)(jm'|ja\Gamma\gamma)^* = \delta_{mm'} \tag{82}$$

Observe that (78) and (79) are note 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

$$(jm|jb\Gamma\gamma) := \sum_{a}(jm|ja\Gamma\gamma)M_{ab} \tag{83}$$

where M is an arbitrary unitary matrix satisfy (78) and (79) with the replacement $a \to b$. Nevertheless, (78) and (79) lead to systems that may be useful for the calculation of the $(jm|ja\Gamma\gamma)$ coefficients.

2 - Irreducible tensorial sets

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

$$|\tau ja\Gamma\gamma) := \sum_{m}|\tau jm)(jm|ja\Gamma\gamma) \tag{84}$$

60

Equation (79) allows us to show

$$P_R|\tau j a \Gamma \gamma) = \sum_{\gamma'} |\tau j a \Gamma \gamma') D^\Gamma(R)_{\gamma'\gamma} \tag{85}$$

for any R in G^*. Similarly, from the ITS of operators $\{T_q^{(k)} : q = k, k-1, \ldots, -k\}$ associated with $\mathbf{D}^{(k)}$, we define

$$T_\gamma^{(ka\Gamma)} \equiv T_{a\Gamma\gamma}^{(k)} := \sum_q T_q^{(k)}(kq|ka\Gamma\gamma) \tag{86}$$

so that

$$P_R T_\gamma^{(ka\Gamma)} P_R^{-1} = \sum_{\gamma'} T_{\gamma'}^{(ka\Gamma)} D^\Gamma(R)_{\gamma'\gamma} \tag{87}$$

holds for any R in G^*.

At this point, it is important to remark that (84) and (86) provide us with ITSs both for $SU(2)$ and G^*. Indeed $\{|\tau j a \Gamma \gamma) : \gamma$ ranging $\}$ is an ITS of vectors spanning the matrix representation D^Γ of G^* while $\{|\tau j a \Gamma \gamma) : a\Gamma\gamma$ ranging $\}$ is an ITS of vectors spanning the matrix representation $\mathcal{D}^{(j)}$ of $SU(2)$ defined by

$$\mathcal{D}^{(j)}(R)_{a\Gamma\gamma,a'\Gamma'\gamma'} := \sum_{mm'} (jm|ja\Gamma\gamma)^* D^{(j)}(R)_{mm'}(jm'|ja'\Gamma'\gamma') \tag{88}$$

for any R in $SU(2)$. A similar remark applies to the sets $\{T_\gamma^{(ka\Gamma)} : \gamma$ ranging $\}$ and $\{T_{a\Gamma\gamma}^{(k)} : a\Gamma\gamma$ 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, (62) gives

$$
\begin{aligned}
(\tau_1 j_1 a_1 \Gamma_1 \gamma_1 | T_\gamma^{(ka\Gamma)} | \tau_2 j_2 a_2 \Gamma_2 \gamma_2) &= \sum_\rho (\tau_1 j_1 a_1 \Gamma_1 || T^{(ka\Gamma)} || \tau_2 j_2 a_2 \Gamma_2)_\rho \\
&\times \sum_{\Gamma_1'\gamma_1'} \begin{pmatrix} \Gamma_1' & \Gamma_1 \\ \gamma_1' & \gamma_1 \end{pmatrix} \begin{pmatrix} \Gamma & \Gamma_2 & \Gamma_1' \\ \gamma & \gamma_2 & \gamma_1' \end{pmatrix}_\rho^*
\end{aligned} \tag{89}
$$

For $SU(2)$ in a $SU(2) \supset G^*$ basis, we can combine (63), (84) and (86) to obtain the compact formula

$$(\tau_1 j_1 a_1 \Gamma_1 \gamma_1 | T_{a\Gamma\gamma}^{(k)} | \tau_2 j_2 a_2 \Gamma_2 \gamma_2) = (\tau_1 j_1 || T^{(k)} || \tau_2 j_2) f \begin{pmatrix} j_1 & j_2 & k \\ a_1\Gamma_1\gamma_1 & a_2\Gamma_2\gamma_2 & a\Gamma\gamma \end{pmatrix} \tag{90}$$

where the f symbol is defined by

$$f \begin{pmatrix} j_1 & j_2 & k \\ a_1\Gamma_1\gamma_1 & a_2\Gamma_2\gamma_2 & a\Gamma\gamma \end{pmatrix} := (-1)^{2k}(2j_1+1)^{-1/2}(j_2 k a_2 \Gamma_2 \gamma_2 a\Gamma\gamma | j_1 a_1 \Gamma_1 \gamma_1)^* \tag{91}$$

in function of the CGC

$$
\begin{aligned}
(j_1 j_2 a_1 \Gamma_1 \gamma_1 a_2 \Gamma_2 \gamma_2 | j a \Gamma \gamma) &:= \sum_{m_1 m_2 m} (j_1 m_1 | j_1 a_1 \Gamma_1 \gamma_1)^* \\
&\times (j_2 m_2 | j_2 a_2 \Gamma_2 \gamma_2)^* (j_1 j_2 m_1 m_2 | jm)(jm|ja\Gamma\gamma)
\end{aligned} \tag{92}
$$

61

of $SU(2)$ in a $SU(2) \supset G^*$ basis [26].

There are many advantages to use (90) rather than (89). In (89), both the reduced matrix elements and the coupling coefficients (cf., the $2-a\alpha$ and $(3-a\alpha)_\rho$ symbols) depend of the symmetry group G^*. Furthermore, the factorization offered by (89) is not complete in view of the summation over the multiplicity label ρ. On the other side, the matrix element given by (90) factorizes in two parts: a coupling coefficient (cf., the f symbol) for the $SU(2) \supset G^*$ chain 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 (90) 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 (90) most of the time concerns the f geometrical coefficient, 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 $\mathbf{U}^k$ of the same rank.

The calculation of the f coefficients defined by (91) and (92) touches a simple problem of symmetry adaptation. In fact, the determination of the symmetry-adapted CGCs (92) require the knowledge of the reduction coefficients (80). These reduction coefficients are the expansion coefficients of symmetry adapted functions (cf., (84)) or symmetry-adapted operators (cf., (86) so that their calculation may be achieved by numerous means (resolution of linear systems like (78) or (79), projection operator techniques, ...).

4 - The $\bar{f}$ symbol

Equation (91) shows that the behavior 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 $1-ja\Gamma\gamma$ symbol

$$\begin{pmatrix} & j & \\ a\Gamma\gamma & & a'\Gamma'\gamma' \end{pmatrix} := \sum_{mm'} (jm|ja\Gamma\gamma)^* \begin{pmatrix} & j & \\ m & & m' \end{pmatrix} (jm'|ja'\Gamma'\gamma')^* \tag{93}$$

where the $1-jm$ symbol is defined by (67) and (68). The $\bar{f}$ or $3-ja\Gamma\gamma$ symbol defined through

$$\begin{aligned} \bar{f} \begin{pmatrix} j_1 & j_2 & j_3 \\ a_1\Gamma_1\gamma_1 & a_2\Gamma_2\gamma_2 & a_3\Gamma_3\gamma_3 \end{pmatrix} &:= \sum_{a_4\Gamma_4\gamma_4} \begin{pmatrix} & j_3 & \\ a_3\Gamma_3\gamma_3 & & a_4\Gamma_4\gamma_4 \end{pmatrix} \\ &\times f \begin{pmatrix} j_3 & j_2 & j_1 \\ a_4\Gamma_4\gamma_4 & a_2\Gamma_2\gamma_2 & a_1\Gamma_1\gamma_1 \end{pmatrix}^* \end{aligned} \tag{94}$$

then exhibits a high (permutation) symmetry since a simple development of (94) leads to

$$\bar{f} \begin{pmatrix} j_1 & j_2 & j_3 \\ a_1\Gamma_1\gamma_1 & a_2\Gamma_2\gamma_2 & a_3\Gamma_3\gamma_3 \end{pmatrix} = \sum_{m_1m_2m_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \prod_{i=1}^{3} (j_im_i|j_ia_i\Gamma_i\gamma_i)^* \tag{95}$$

(see [26]).

For $G^* \equiv U(1)$ the $\bar{f}$ symbol and the $1-ja\Gamma\gamma$ symbol reduce to the $3-jm$ Wigner symbol and to the $1-jm$ Herring-Wigner symbol, respectively. The $1-ja\Gamma\gamma$ and $\bar{f}$ symbols are thus $2-a\alpha$

and 3–$a\alpha$ symbols as defined in Sec. II (with $a \to j$ and $\alpha \to a\Gamma\gamma$), respectively, for the group $SU(2)$ in a $SU(2) \supset G^*$ basis. The properties (existence conditions, selection rules, symmetry properties, orthogonality relations, ...) 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 [26, 27, 28]. Let us simply mention that, by applying Racah's lemma, the $\bar{f}$ symbol can be developed as a linear combination of $(3–\Gamma\gamma)_\rho$ according to

$$\bar{f}\begin{pmatrix} j_1 & j_2 & j_3 \\ a_1\Gamma_1\gamma_1 & a_2\Gamma_2\gamma_2 & a_3\Gamma_3\gamma_3 \end{pmatrix} = \sum_\rho \bar{f}\left(\begin{pmatrix} j_1 & j_2 & j_3 \\ a_1\Gamma_1 & a_2\Gamma_2 & a_3\Gamma_3 \end{pmatrix}\right)_\rho \begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix}_\rho \quad (96)$$

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

We are now in a position to enunciate correspondence rules for passing from the Wigner-Racah algebra of $SU(2)$ in a $SU(2) \supset U(1)$ basis (i.e., in the $\{jm\}$ scheme) to the Wigner-Racah algebra of $SU(2)$ in a $SU(2) \supset G^*$ basis (i.e., in the $\{ja\Gamma\gamma\}$ scheme): All the m- or q-dependent quantities are replaced by the corresponding $a\Gamma\gamma$-dependent quantities while the basis-independent quantities (like 6–j and 9–j symbols) are unchanged. More precisely, we have

$$
\begin{aligned}
D^{(j)}(R)_{mm'} &\to \mathcal{D}^{(j)}_{a\Gamma\gamma,a'\Gamma'\gamma'} \\
(j_1 j_2 m_1 m_2 | jm) &\to (j_1 j_2 a_1\Gamma_1\gamma_1 a_2\Gamma_2\gamma_2 | ja\Gamma\gamma) \\
1{-}jm \text{ symbol} &\to 1{-}a\Gamma\gamma \text{ symbol} \\
3{-}jm \text{ symbol} &\to \bar{f} \text{ symbol} \\
3(n-1){-}j \text{ symbol} &\to 3(n-1){-}j \text{ symbol} \\
|\tau jm) &\to |\tau j a\Gamma\gamma) \\
T^{(k)}_q &\to T^{(k)}_{a\Gamma\gamma}
\end{aligned}
\quad (97)
$$

(see [27] for more details).

3.9.3 The G^* group in a $G^* \subset SU(2)$ basis

1 - The general case

Equations (32)-(36) were used in numerous works for calculating coupling coefficients and V symbols of subgroups of $SU(2)$. (Following Griffith [45], the $(3–a\alpha)_\rho$ symbols of a group of molecular interest are referred to as V symbols in what follows.) 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 $SU(2) \supset G^*$ chain. This method combines three basic ingredients scattered in various (implicit or explicit) approaches starting with the pioneer works by Tanabe, Sugano and Kamimura: the concept of quasi angular momentum, the definition of the $\bar{f}$ symbol and renormalization techniques. 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 Γ IRC of G^*, let $(\hat{\jmath}(\Gamma))$ or simply $(\hat{\jmath})$ be the IRC of $SU(2)$ that contains Γ once and only once. Thus, $\hat{\jmath}$ is the smallest value of j for which $\sigma(\Gamma|j) = 1$. The value $\hat{\jmath}$ refers to a

quasi angular momentum [111] (see [109] too). In the multiplicity-free case where the identity IRC of G^* appears once and 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

$$
\begin{aligned}
V \begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix} &:= x(\Gamma_1\Gamma_2\Gamma_3) \bar{f} \begin{pmatrix} \hat{j}_1 & \hat{j}_2 & \hat{j}_3 \\ \Gamma_1\gamma_1 & \Gamma_2\gamma_2 & \Gamma_3\gamma_3 \end{pmatrix} \\
&\times \left[\sum_{\gamma_1\gamma_2\gamma_3} \left| \bar{f} \begin{pmatrix} \hat{j}_1 & \hat{j}_2 & \hat{j}_3 \\ \Gamma_1\gamma_1 & \Gamma_2\gamma_2 & \Gamma_3\gamma_3 \end{pmatrix} \right|^2 \right]^{-1/2}
\end{aligned}
\tag{98}
$$

where $x(\Gamma_1\Gamma_2\Gamma_3)$ is an a arbitrary phase factor that depends on Γ_1, Γ_2 and Γ_3 only. It can be verified by repeated application of (96) that the V symbol defined by (98) satisfies (49) and (50) for G^*. Consequently, the V symbol is nothing but a 3–$\Gamma\gamma$ symbol for the G^* group compatible with the choice implicitly assumed through (95) with $j = \hat{j}(\Gamma)$ for the representation matrices D^Γ.

For the sake of simplifying calculations with (98), it should be noted that

$$
\sum_{\gamma_1\gamma_2\gamma_3} \left| \bar{f} \begin{pmatrix} \hat{j}_1 & \hat{j}_2 & \hat{j}_3 \\ \Gamma_1\gamma_1 & \Gamma_2\gamma_2 & \Gamma_3\gamma_3 \end{pmatrix} \right|^2 = [\Gamma_i] \sum_{\text{all } \gamma_k \text{ except } \gamma_i} \left| \bar{f} \begin{pmatrix} \hat{j}_1 & \hat{j}_2 & \hat{j}_3 \\ \Gamma_1\gamma_1 & \Gamma_2\gamma_2 & \Gamma_3\gamma_3 \end{pmatrix} \right|^2
\tag{99}
$$

for $i = 1$, 2 or 3. In addition, if two of the three Γ's are equivalent to two of the corresponding three $(\hat{j})$'s, the right-hand side of (99) can be simplified and (98) takes a simple form. For instance, in the case $(\hat{j}_1) \equiv \Gamma_1$ and $(\hat{j}_2) \equiv \Gamma_2$, (98) becomes

$$
V \begin{pmatrix} \Gamma_1 & \Gamma_2 & \Gamma_3 \\ \gamma_1 & \gamma_2 & \gamma_3 \end{pmatrix} = x(\Gamma_1\Gamma_2\Gamma_3)[\Gamma_3]^{-1/2}(2\hat{j}_3 + 1)^{1/2} \bar{f} \begin{pmatrix} \hat{j}_1 & \hat{j}_2 & \hat{j}_3 \\ \Gamma_1\gamma_1 & \Gamma_2\gamma_2 & \Gamma_3\gamma_3 \end{pmatrix}
\tag{100}
$$

which is very simple to handle.

The main advantages of the method based on (98)-(100) 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 deduced from a minimal set of $\bar{f}$ coefficients which are readily calculated (by hand or with the help of a computer) from (95). The thus obtained V coefficients of the G^* group are simple linear combinations of 3–jm coefficients for the $SU(2) \supset U(1)$ chain. Second, such a method allows us to work with bases of interest for molecular physics and quantum chemistry. In this respect, we may use in (95) reduction coefficients $(jm|ja\Gamma\gamma)$ corresponding to Cartesian p, d and f spin-orbitals or corresponding to a chain of groups (for instance, the $SU(2) \supset O^* \supset D_4^* \supset D_2^*$ tetragonal chain or the $SU(2) \supset O^* \supset D_3^* \supset C_3^*$ trigonal chain). Third, it is possible to transfer some of the features (formulas, symmetry properties, ...) of the 3–jm symbol from the $SU(2) \supset U(1)$ standard chain to the V symbol of G^*. For example, the permutation symmetry properties of the V symbol can be chosen to be essentially the ones of the 3–jm symbol. In fact, by choosing $x(\Gamma_1\Gamma_2\Gamma_3)$ invariant under the 3! permutations of its arguments, the V symbol given by (98)-(100) is multiplied by $(-1)^{\hat{j}_1(\Gamma_1)+\hat{j}_2(\Gamma_2)+\hat{j}_3(\Gamma_3)}$ under an odd permutation of its columns so that is is invariant under an even permutation.

2 - Application to the octahedral group

As an illustration, we consider the case where G^* is the O^* double octahedral group and limit ourselves to the determination of the V coefficients of the O octahedral group. Therefore, we can replace $SU(2) \supset O^*$ by $SO(3) \supset O$. The restriction of $SO(3)$ to O yields

$$\hat{\jmath}(A_1) = 0, \quad \hat{\jmath}(A_2) = 3, \quad \hat{\jmath}(E) = 2, \quad \hat{\jmath}(T_1) = 1, \quad \hat{\jmath}(T_2) = 2 \tag{101}$$

where A_1, A_2, E, T_1 and T_2 denote the various IRCs of O. In view of the permutation symmetry properties of the V symbol, there are *a priori* 39 independent V coefficients to be calculated for the O group. The $|\hat{\jmath}\Gamma\gamma)$ vectors (the label a is not necessary here) required for calculating these coefficients are given by

$$
\begin{aligned}
|0A_1a_1) &= |0,0) \\
|3A_2a_2) &= \frac{1}{\sqrt{2}}[|3,2) - |3,-2)] \\
|2E\theta) &= |2,0), \quad |2E\epsilon) = \frac{1}{\sqrt{2}}[|2,2) + |2,-2)] \\
|1T_1x) &= -\frac{i}{\sqrt{2}}[|1,1) - |1,-1)] \\
|1T_1y) &= \frac{1}{\sqrt{2}}[|1,1) + |1,-1)] \\
|1T_1z) &= i|1,0) \\
|2T_2x) &= \frac{i}{\sqrt{2}}[|2,1) + |2,-1)] \\
|2T_2y) &= \frac{1}{\sqrt{2}}[|2,1) - |2,-1)] \\
|2T_2z) &= -\frac{i}{\sqrt{2}}[|2,2) - |2,-2)]
\end{aligned}
\tag{102}
$$

in terms of spherical basis vectors $|j,m)$ (the generic symbol γ is a_1 for A_1; a_2 for A_2; θ and ϵ for E; x, y and z for T_1; and x, y and z for T_2). The 39 independent V coefficients are then easily calculated from (95) and (98)-(102). They are of course all real if we replace the pure imaginary number i by 1 in (102). In the case $i = \sqrt{-1}$, it is possible to decrease the number of independent V coefficients by conveniently choosing the $x(\Gamma_1\Gamma_2\Gamma_3)$ phase factors. Along this line, by taking $i = \sqrt{-1}$ and $x(\Gamma_1\Gamma_2\Gamma_3) = 1$ except $x(ET_2T_2) = x(T_1T_1T_1) = x(T_1T_1T_2) = x(T_2T_2T_2) = -1$, the reader will verify that Eqs. (95) and (98)-(102) lead to the real numerical values obtained by Griffith [45] for the V coefficients of O in his real tetragonal component system.

It should be noted that each V coefficient calculated from (95) and (98)-(102) can be reduced (up to a multiplicative factor) to a single 3–jm coefficient for the $SO(3) \supset SO(2)$ chain. We thus foresee that some properties of certain 3–jm symbols for the $SU(2) \supset U(1)$ chain may be derived by looking at some properties induced by a subgroup of $SU(2)$. As an example, we have

$$V\begin{pmatrix} A_2 & A_2 & E \\ a_2 & a_2 & \theta \end{pmatrix} \sim \bar{f} \begin{pmatrix} 3 & 3 & 2 \\ A_2a_2 & A_2a_2 & E\theta \end{pmatrix} = -\begin{pmatrix} 3 & 3 & 2 \\ -2 & 2 & 0 \end{pmatrix} \tag{103}$$

It is clear that the value of the V coefficient in (103) is zero since the $A_2 \otimes A_2 \otimes E$ triple Kronecker product does not contain the A_1 IRC of the O group. As a consequence, the 3–jm symbol in (103) corresponding to the $SU(2) \supset U(1)$ chain vanishes (owing to a selection rule for O) in

spite of the fact that the (trivial and Regge) symmetry properties for $SU(2) \supset U(1)$ do not impose such a result.

To close Section 3, it is to be mentioned that diagrammatic methods initially developed for simplifying calculations within the Wigner-Racah algebra of the rotation group [112] where extended to the case of a finite or compact group [113, 114, 115]. Note also that considerable attention was paid in the nineties to the Wigner-Racah calculus for a q-deformed finite or compact group (see [116] for some general considerations on this subject and [117, 118, 119] for some developments on $U_q(su(2))$ and $U_q(su(3)))$.

4   Contact with quantum information

4.1   *Computational basis and standard $SU(2)$ basis*

In quantum information, we use qubits which are nothing but state vectors in the Hilbert space $\mathbb{C}^2$. The more general qubit

$$|\psi_2\rangle := c_0|0\rangle + c_1|1\rangle, \quad c_0 \in \mathbb{C}, \quad c_1 \in \mathbb{C}, \quad |c_0|^2 + |c_1|^2 = 1 \tag{104}$$

is a linear combination of the vectors $|0\rangle$ and $|1\rangle$ which constitute an orthonormal basis

$$B_2 := \{|0\rangle, |1\rangle\} \tag{105}$$

of $\mathbb{C}^2$. The two vectors $|0\rangle$ and $|1\rangle$ can be considered as the basis vectors for the fundamental IRC of $SU(2)$, in the $SU(2) \supset U(1)$ scheme, corresponding to $j = 1/2$ with

$$|0\rangle \equiv |1/2, 1/2\rangle, \quad |1\rangle \equiv |1/2, -1/2\rangle \tag{106}$$

More generally, in dimension d we use qudits of the form

$$|\psi_d\rangle := \sum_{n=0}^{d-1} c_n|n\rangle, \quad c_n \in \mathbb{C}, \quad n = 0, 1, \ldots, d-1, \quad \sum_{n=0}^{d-1} |c_n|^2 = 1 \tag{107}$$

in terms of the orthonormal basis

$$B_d := \{|n\rangle : n = 0, 1, \ldots, d-1\} \tag{108}$$

of $\mathbb{C}^d$. By introducing

$$j := \frac{1}{2}(d-1), \quad m := n - \frac{1}{2}(d-1), \quad |j, m\rangle := |d-1-n\rangle \tag{109}$$

the vectors $|n\rangle$ can be viewed as the basis vectors for the (j) IRC of $SU(2)$ in the $SU(2) \supset U(1)$ scheme. In this scheme, the $|j, m\rangle$ vector is a common eigenvector of the Casimir operator J^2 (the square of an angular momentum) and of a Cartan generator J_z (the z component of the angular momentum) of the $su(2)$ Lie algebra. More precisely, we have the relations

$$J^2|j, m\rangle = j(j+1)|j, m\rangle, \quad J_z|j, m\rangle = m|j, m\rangle \tag{110}$$

66

which are familiar in angular momentum theory. In other words, the basis B_d, known in quantum information as the computational basis, can be visualized as the $SU(2) \supset U(1)$ standard basis or angular momentum basis

$$B_{2j+1} := \{|j, m\rangle : m = j, j-1, \ldots, -j\} \tag{111}$$

with the correspondence

$$|0\rangle \equiv |j, j\rangle, \quad |1\rangle \equiv |j, j-1\rangle, \quad \ldots, \quad |d-1\rangle \equiv |j, -j\rangle \tag{112}$$

between qudits and angular momentum states.

4.2 Nonstandard SU(2) basis

We are now in a position to introduce nonstandard $SU(2)$ bases which shall be connected in the next subsection to the so-called mutually unbiased bases (MUBs) of quantum information. As far as the representation theory of $SU(2)$ is concerned, we can replace the set $\{J^2, J_z\}$ by another complete set of two commuting operators. Following [120], we consider the commuting set $\{J^2, v_{ra}\}$, where the operator v_{ra} is defined by

$$v_{ra} := e^{i2\pi jr}|j, -j\rangle\langle j, j| + \sum_{m=-j}^{j-1} q^{(j-m)a}|j, m+1\rangle\langle j, m| \tag{113}$$

modulo its action on the space of constant angular momentum j spanned by the B_{2j+1} basis. In (113), q is a primitive $(2j+1)$-th root of unity, i.e.,

$$q := e^{2\pi i/(2j+1)} \tag{114}$$

and the parameters r and a are fixed parameters such that

$$r \in \mathbb{R}, \quad a \in \mathbb{Z}/(2j+1)\mathbb{Z} \tag{115}$$

It is to be noted that v_{ra} is pseudo-invariant under the cyclic group C_{2j+1} in the sense that it transforms as an IRC of C_{2j+1} (different from the identity IRC). The common eigenstates of J^2 and v_{ra}, associated with the $SO(3) \supset C_{2j+1}$ chain, provide an alternative basis to that given by the common eigenstates of J^2 and J_z, associated with the $SO(3) \supset SO(2)$ chain. This can be made precise by the following result.

Theorem 3. For fixed j, r and a, the $2j + 1$ common eigenvectors of v_{ra} and J^2 can be taken in the form

$$|j\alpha; ra\rangle = \frac{1}{\sqrt{2j+1}} \sum_{m=-j}^{j} q^{(j+m)(j-m+1)a/2-jmr+(j+m)\alpha}|j, m\rangle \tag{116}$$

with $\alpha = 0, 1, \ldots, 2j$. The corresponding eigenvalues of v_{ra} are given by

$$v_{ra}|j\alpha; ra\rangle = q^{j(r+a)-\alpha}|j\alpha; ra\rangle \tag{117}$$

so that the spectrum of v_{ra} is non degenerate.

The inner product

$$\langle j\alpha; ra|j\beta; ra\rangle = \delta_{\alpha,\beta} \tag{118}$$

shows that

$$B_{ra} := \{|j\alpha; ra\rangle : \alpha = 0, 1, \ldots, 2j\} \tag{119}$$

is an orthonormal set which provides a nonstandard basis for the irreducible representation matrix of $SU(2)$ associated with j. For fixed j, there exists a $(2j + 1)$-multiple infinity of orthonormal bases B_{ra} since r can have any real value and a, which belongs to the ring $\mathbb{Z}/(2j + 1)\mathbb{Z}$, can take $2j + 1$ distinct values ($a = 0, 1, \ldots, 2j$).

4.3 Other bases in quantum information

We now go back to quantum information. By using the change of notations

$$d := 2j + 1, \quad n := j + m, \quad |n\rangle := |j, -m\rangle, \quad |a\alpha; r\rangle := |j\alpha; ra\rangle \tag{120}$$

adapted to quantum information and in agreement with (109), the operator v_{ra} can be rewritten as

$$v_{ra} = e^{i\pi(d-1)r}|d - 1\rangle\langle 0| + \sum_{n=1}^{d-1} q^{na}|n - 1\rangle\langle n| \tag{121}$$

Each of the eigenvectors

$$|a\alpha; r\rangle = q^{(d-1)^2 r/4}\frac{1}{\sqrt{d}}\sum_{n=0}^{d-1} q^{n(d-n)a/2+n[\alpha-(d-1)r/2]}|d - 1 - n\rangle \tag{122}$$

(with $\alpha = 0, 1, \ldots, d - 1$) of v_{ra} is a linear combination of the qudits $|0\rangle, |1\rangle, \ldots, |d - 1\rangle$. For fixed d, r and a, the orthonormal basis

$$B_{ra} := \{|a\alpha; r\rangle : \alpha = 0, 1, \ldots, d - 1\} \tag{123}$$

is an alternative to the B_d computational basis. As already mentioned, there is d-multiple infinity of orthonormal bases B_{ra}.

All this can be transcribed in terms of matrices. Let V_{ra} be the $d \times d$ matrix of the operator v_{ra}. The unitary matrix V_{ra}, built on the basis B_d with the ordering $0, 1, \ldots, d - 1$ for the lines and columns, reads

$$V_{ra} = \begin{pmatrix} 0 & q^a & 0 & \ldots & 0 \\ 0 & 0 & q^{2a} & \ldots & 0 \\ \vdots & \vdots & \vdots & \ldots & \vdots \\ 0 & 0 & 0 & \ldots & q^{(d-1)a} \\ e^{i\pi(d-1)r} & 0 & 0 & \ldots & 0 \end{pmatrix} \tag{124}$$

The eigenvectors of V_{ra} are

$$\phi(a\alpha;r) = q^{(d-1)^2 r/4} \frac{1}{\sqrt{d}} \sum_{n=0}^{d-1} q^{n(d-n)a/2 - n(d-1)r/2 + n\alpha} \phi_{d-1-n} \tag{125}$$

(with $\alpha = 0, 1, \ldots, d-1$), where the ϕ_k with $k = 0, 1, \ldots, d-1$ are the column vectors

$$\phi_0 := \begin{pmatrix} 1 \\ 0 \\ \vdots \\ 0 \end{pmatrix}, \quad \phi_1 := \begin{pmatrix} 0 \\ 1 \\ \vdots \\ 0 \end{pmatrix}, \quad \ldots, \quad \phi_{d-1} := \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 1 \end{pmatrix} \tag{126}$$

representing the qudits $|0\rangle, |1\rangle, \ldots, |d-1\rangle$, respectively. They satisfy the eigenvalue equation

$$V_{ra}\phi(a\alpha;r) = q^{(d-1)(r+a)/2 - \alpha}\phi(a\alpha;r) \tag{127}$$

with $\alpha = 0, 1, \ldots, d-1$. The V_{ra} matrix can be diagonalized by means of the H_{ra} unitary matrix of elements

$$(H_{ra})_{n\alpha} := \frac{1}{\sqrt{d}} q^{(d-1-n)(n+1)a/2 + (d-1)^2 r/4 + (d-1-n)[\alpha - (d-1)r/2]} \tag{128}$$

with the lines and columns of H_{ra} arranged from left to right and from top to bottom in the order $n, \alpha = 0, 1, \ldots, d-1$. Indeed, we have

$$(H_{ra})^\dagger V_{ra} H_{ra} = q^{(d-1)(r+a)/2} \begin{pmatrix} q^0 & 0 & \ldots & 0 \\ 0 & q^{-1} & \ldots & 0 \\ \vdots & \vdots & \ldots & \vdots \\ 0 & 0 & \ldots & q^{-(d-1)} \end{pmatrix} \tag{129}$$

in agreement with (127). As an illustration, let us consider the $d = 2$ and $d = 3$ cases.

For $d = 2$, we have two families of bases: the B_{r0} family and the B_{r1} family (a can take the values $a = 0$ and $a = 1$). The matrix (see (124))

$$V_{ra} := \begin{pmatrix} 0 & q^a \\ e^{i\pi r} & 0 \end{pmatrix}, \quad q = e^{i\pi} \tag{130}$$

has the eigenvectors (see (125))

$$\phi(a\alpha;r) = \frac{1}{\sqrt{2}}(q^{a/2 - r/4 + \alpha}\phi_0 + q^{r/4}\phi_1), \quad \alpha = 0, 1 \tag{131}$$

which correspond to the basis B_{ra}. For $r = 0$, the bases

$$B_{00}: \quad \phi(00;0) = \frac{1}{\sqrt{2}}(\phi_1 + \phi_0), \quad \phi(01;0) = \frac{1}{\sqrt{2}}(\phi_1 - \phi_0) \tag{132}$$

$$B_{01}: \quad \phi(10;0) = \frac{1}{\sqrt{2}}(\phi_1 + i\phi_0), \quad \phi(11;0) = \frac{1}{\sqrt{2}}(\phi_1 - i\phi_0) \tag{133}$$

are (up to a rearrangement) familiar bases for qubits.

For $d = 3$, we have three families of bases, that is to say B_{r0}, B_{r1} and B_{r2}, since a can be 0, 1 and 2. In this case, the matrix

$$V_{ra} := \begin{pmatrix} 0 & q^a & 0 \\ 0 & 0 & q^{2a} \\ e^{i\pi 2r} & 0 & 0 \end{pmatrix}, \quad q = e^{i2\pi/3} \tag{134}$$

admits the eigenvectors

$$\phi(a\alpha; r) = \frac{1}{\sqrt{3}} q^r \left(q^{a+2\alpha-2r}\phi_0 + q^{a+\alpha-r}\phi_1 + \phi_2 \right), \quad \alpha = 0, 1, 2 \tag{135}$$

For $r = 0$, the bases

$$B_{00} : \quad \phi(00; 0) = \frac{1}{\sqrt{3}} \left(\phi_2 + \phi_1 + \phi_0 \right)$$

$$\phi(01; 0) = \frac{1}{\sqrt{3}} \left(\phi_2 + q\phi_1 + q^2\phi_0 \right) \tag{136}$$

$$\phi(02; 0) = \frac{1}{\sqrt{3}} \left(\phi_2 + q^2\phi_1 + q\phi_0 \right)$$

$$B_{01} : \quad \phi(10; 0) = \frac{1}{\sqrt{3}} \left(\phi_2 + q\phi_1 + q\phi_0 \right)$$

$$\phi(11; 0) = \frac{1}{\sqrt{3}} \left(\phi_2 + q^2\phi_1 + \phi_0 \right) \tag{137}$$

$$\phi(12; 0) = \frac{1}{\sqrt{3}} \left(\phi_2 + \phi_1 + q^2\phi_0 \right)$$

$$B_{02} : \quad \phi(20; 0) = \frac{1}{\sqrt{3}} \left(\phi_2 + q^2\phi_1 + q^2\phi_0 \right)$$

$$\phi(21; 0) = \frac{1}{\sqrt{3}} \left(\phi_2 + \phi_1 + q\phi_0 \right) \tag{138}$$

$$\phi(22; 0) = \frac{1}{\sqrt{3}} \left(\phi_2 + q\phi_1 + \phi_0 \right)$$

are useful for qutrits.

4.4 Mutually unbiased bases

Going back to the case where d is arbitrary, we now examine an important property of the couple (B_{ra}, B_d) and its generalization to couples (B_{ra}, B_{rb}) with $b \neq a$. For fixed d, r and a, (122) gives

$$\forall n, \alpha \in \{0, 1, \ldots, d-1\} : |\langle n|a\alpha; r\rangle| = \frac{1}{\sqrt{d}} \tag{139}$$

Equation (139) shows that B_{ra} and B_d are two unbiased bases. (Let us recall that two distinct orthonormal bases $B_a = \{|a\alpha\rangle : \alpha = 0, 1, \ldots, d-1\}$ and $B_b = \{|b\beta\rangle : \beta = 0, 1, \ldots, d-1\}$ of the Hilbert space $\mathbb{C}^d$ are said to be unbiased if and only if the inner product $\langle a\alpha|b\beta\rangle$ has a modulus independent of α and β.)

Other examples of unbiased bases can be obtained for $d = 2$ and 3. We easily verify that the bases B_{r0} and B_{r1} for $d = 2$ given by (131) are unbiased. Similarly, the bases B_{r0}, B_{r1} and B_{r2}

for $d = 3$ given by (135) are mutually unbiased. Therefore, by combining these particular results with the general result implied by (139) we end up with 3 mutually unbiased bases (MUBs) for $d = 2$ and 4 MUBs for $d = 3$. This is in agreement with the theorem according to which the number N_{MUB} of pairwise MUBs in $\mathbb{C}^d$ is such that $3 \leq N_{MUB} \leq d + 1$ and that the maximum number $d + 1$ is attained when d is a prime number p or an integer power p^e ($e \geq 2$) of a prime number p [121, 122, 123]. The results for $d = 2$ and 3 can be generalized in the case where d is a prime number. This can be precised by the following theorem [124, 125, 126, 127, 128].

Theorem 4. For $d = p$, with p a prime number, the bases $B_{r0}, B_{r1}, \ldots, B_{rp-1}, B_p$ corresponding to a fixed value of r form a complete set of $p + 1$ MUBs. The p^2 vectors $|a\alpha; r\rangle$, with $a, \alpha = 0, 1, \ldots, p-1$, of the bases $B_{r0}, B_{r1}, \ldots, B_{rp-1}$ are given by a single formula, namely (122) or (125). The index r makes it possible to distinguish different complete sets of $p + 1$ MUBs.

The proof is as follows. First, according to (139), the computational basis B_p is unbiased with any of the p bases $B_{r0}, B_{r1}, \ldots, B_{rp-1}$. Second, we get

$$\langle a\alpha; r | b\beta; r \rangle = \frac{1}{p} \sum_{k=0}^{p-1} q^{k(p-k)(b-a)/2 + k(\beta - \alpha)} \tag{140}$$

or

$$\langle a\alpha; r | b\beta; r \rangle = \frac{1}{p} \sum_{k=0}^{p-1} e^{i\pi\{(a-b)k^2 + [p(b-a) + 2(\beta - \alpha)]k\}/p} \tag{141}$$

The right-hand side of (141) can be expressed in terms of a generalized quadratic Gauss sum [129]

$$S(u, v, w) := \sum_{k=0}^{|w|-1} e^{i\pi(uk^2 + vk)/w} \tag{142}$$

where u, v and w are integers such that u and w are mutually prime, uw is non vanishing and $uw + v$ is even. This leads to

$$\langle a\alpha; r | b\beta; r \rangle = \frac{1}{p} S(u, v, w) \tag{143}$$

with

$$u := a - b, \quad v := -(a - b)p - 2(\alpha - \beta), \quad w := p \tag{144}$$

The generalized Gauss sum $S(u, v, w)$ in (143)-(144) can be calculated from the methods described in [129]. We thus obtain

$$|\langle a\alpha; r | b\beta; r \rangle| = \frac{1}{\sqrt{p}} \tag{145}$$

which completes the proof.□

4.5 Mutually unbiased bases and Lie algebras

4.5.1 Weyl pairs

The matrix V_{ra} can be decomposed as

$$V_{ra} = P_r X Z^a \tag{146}$$

where

$$P_r := \begin{pmatrix} 1 & 0 & 0 & \dots & 0 \\ 0 & 1 & 0 & \dots & 0 \\ 0 & 0 & 1 & \dots & 0 \\ \vdots & \vdots & \vdots & \dots & \vdots \\ 0 & 0 & 0 & \dots & e^{i\pi(d-1)r} \end{pmatrix} \tag{147}$$

and

$$X := \begin{pmatrix} 0 & 1 & 0 & \dots & 0 \\ 0 & 0 & 1 & \dots & 0 \\ \vdots & \vdots & \vdots & \dots & \vdots \\ 0 & 0 & 0 & \dots & 1 \\ 1 & 0 & 0 & \dots & 0 \end{pmatrix}, \quad Z := \begin{pmatrix} 1 & 0 & 0 & \dots & 0 \\ 0 & q & 0 & \dots & 0 \\ 0 & 0 & q^2 & \dots & 0 \\ \vdots & \vdots & \vdots & \dots & \vdots \\ 0 & 0 & 0 & \dots & q^{d-1} \end{pmatrix} \tag{148}$$

The linear operators corresponding to the matrices X and Z are known in quantum information as shift and clock operators, respectively. The unitary matrices X and Z q-commute in the sense that

$$XZ - qZX = 0 \tag{149}$$

In addition, they satisfy

$$X^d = Z^d = I_d \tag{150}$$

where I_d is the d-dimensional unit matrix. Equations (149) and (150) show that X and Z constitute a Weyl pair [130]. The (X, Z) Weyl pair turns out to be an integrity basis for generating a set $\{X^a Z^b : a, b = 0, 1, \dots, d-1\}$ of d^2 generalized Pauli matrices in d dimensions (see for instance [127, 131, 132, 133] in the context of MUBs and [134, 135, 136] in group-theoretical contexts). In addition, the set $\{q^a X^b Z^c : a, b, c = 0, 1, \dots, d-1\}$ generates, with respect to matrix multiplication, a finite group of order d^3, the P_d Pauli group [127]. As an example, for $d = 2$ we have

$$X = \sigma_x, \quad Z = \sigma_z, \quad XZ = -i\sigma_y, \quad X^0 Z^0 = \sigma_0 \tag{151}$$

in terms of the ordinary Pauli matrices $\sigma_0 = I_2$, σ_x, σ_y and σ_z, and the Pauli group P_2 is isomorphic with the hyperbolic quaternion group.

Equations (149) and (150) can be generalized through

$$V_{ra} Z - qZV_{ra} = 0, \quad e^{-i\pi(d-1)(r+a)} (V_{ra})^d = Z^d = I_d \tag{152}$$

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so that other pairs of Weyl can be obtained from V_{ra} and Z. Note that

$$X = V_{00}, \quad Z = (V_{00})^\dagger \, V_{01} \tag{153}$$

which shows a further interest of the matrix V_{ra}.

4.5.2   MUBs and the special linear group

In the case where d is a prime integer or a power of a prime integer, it is known that the set $\{X^a Z^b : a, b = 0, 1, \ldots, d-1\} \setminus \{X^0 Z^0\}$ of cardinality $d^2 - 1$ can be partitioned into $d+1$ subsets containing each $d-1$ commuting matrices (cf., [131]). Let us give an example.

For $d = 5$, we have the 6 following sets of 4 commuting matrices

$$
\begin{aligned}
\mathcal{V}_0 &:= \{01, 02, 03, 04\}, & \mathcal{V}_1 &:= \{10, 20, 30, 40\} \\
\mathcal{V}_2 &:= \{11, 22, 33, 44\}, & \mathcal{V}_3 &:= \{12, 24, 31, 43\} \\
\mathcal{V}_4 &:= \{13, 21, 34, 42\}, & \mathcal{V}_5 &:= \{14, 23, 32, 41\}
\end{aligned} \tag{154}
$$

where ab is used as an abbreviation of $X^a Z^b$.

More generally, for $d = p$ with p prime, the $p+1$ sets of $p-1$ commuting matrices are easily seen to be

$$
\begin{aligned}
\mathcal{V}_0 &:= \{X^0 Z^a : a = 1, 2, \ldots, p-1\} \\
\mathcal{V}_1 &:= \{X^a Z^0 : a = 1, 2, \ldots, p-1\} \\
\mathcal{V}_2 &:= \{X^a Z^a : a = 1, 2, \ldots, p-1\} \\
\mathcal{V}_3 &:= \{X^a Z^{2a} : a = 1, 2, \ldots, p-1\} \\
&\;\;\vdots \\
\mathcal{V}_{p-1} &:= \{X^a Z^{(p-2)a} : a = 1, 2, \ldots, p-1\} \\
\mathcal{V}_p &:= \{X^a Z^{(p-1)a} : a = 1, 2, \ldots, p-1\}
\end{aligned} \tag{155}
$$

Each of the $p+1$ sets $\mathcal{V}_0, \mathcal{V}_1, \ldots, \mathcal{V}_p$ can be put in a one-to-one correspondence with one basis of the complete set of $p+1$ MUBs. In fact, $\mathcal{V}_0$ is associated with the computational basis while $\mathcal{V}_1, \mathcal{V}_2, \ldots, \mathcal{V}_p$ are associated with the p remaining MUBs in view of

$$V_{0a} \in \mathcal{V}_{a+1} = \{X^b Z^{ab} : b = 1, 2, \ldots, p-1\}, \quad a = 0, 1, \ldots, p-1 \tag{156}$$

Keeping into account the fact that the set $\{X^a Z^b : a, b = 0, 1, \ldots, p-1\} \setminus \{X^0 Z^0\}$ spans the Lie algebra of the special linear group $SL(p, \mathbb{C})$, we have the following theorem.

Theorem 5. For $d = p$, with p a prime integer, the Lie algebra $sl(p, \mathbb{C})$ of the group $SL(p, \mathbb{C})$ can be decomposed into a sum (vector space sum) of $p+1$ abelian subalgebras each of dimension $p-1$, i.e.

$$sl(p, \mathbb{C}) \simeq v_0 \uplus v_1 \uplus \ldots \uplus v_p \tag{157}$$

where the $p+1$ subalgebras $v_0, v_1, \ldots, v_p$ are Cartan subalgebras generated respectively by the sets $\mathcal{V}_0, \mathcal{V}_1, \ldots, \mathcal{V}_p$ containing each $p-1$ commuting matrices.

The latter result can be extended when $d = p^e$ with p a prime integer and e an integer ($e \geq 2$): there exists a decomposition of $sl(p^e, \mathbb{C})$ into $p^e + 1$ abelian subalgebras of dimension $p^e - 1$ (cf., [128, 136, 137, 138]).

5 Appendix: The Racah parameters

In the case of the ℓ^N configuration, the Coulomb Hamiltonian $\mathcal{H}_C$ can be written as

$$
\mathcal{H}_C = (2\ell + 1)^2 \sum_{k=0,2,\ldots,2\ell} F^k \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 \sum_{i<j} \left(\mathbf{u}^{(k)}(i) \cdot \mathbf{u}^{(k)}(j) \right)
\tag{158}
$$

where the $F^k \equiv D_k(\ell) F_k$ parameters are the usual Slater-Condon-Shortley parameters. It is clear that any linear transformation

$$
\mathcal{E}^\lambda = \sum_{k=0,2,\ldots,2\ell} b(\ell)_{\lambda k} F^k, \quad \lambda = 0, 1, \ldots, \ell
\tag{159}
$$

where $b(\ell)$ is a regular matrix of dimension $\ell + 1$ defines an equally acceptable parametrization.

As a trivial example, the $D[\ldots]$ parametrization in Section 2.5 corresponds to

$$
D[(00)0(kk)00] = (s\|u^{(0)}\|s)^{-2}(\ell\|u^{(k)}\|\ell)^{-2}\sqrt{2k+1}(2\ell+1)^2 \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}^2 F^k
\tag{160}
$$

i.e., to a renormalization of the F^k parameters.

Less trivial examples are provided by the Racah parameters

$$
\begin{aligned}
A &= F^0 - \frac{1}{9}F^4 = F_0 - 49F_4 \\
B &= \frac{1}{441}(9F^2 - 5F^4) = F_2 - 5F_4 \\
C &= \frac{5}{63}F^4 = 35F_4
\end{aligned}
\tag{161}
$$

for the d^N configuration [2] and the Racah parameters

$$
\begin{aligned}
E^0 &= F_0 - 10F_2 - 33F_4 - 286F_6 \\
E^1 &= \frac{1}{9}(70F_2 + 231F_4 + 2002F_6) \\
E^2 &= \frac{1}{9}(F_2 - 3F_4 + 7F_6) \\
E^3 &= \frac{1}{3}(5F_2 + 6F_4 - 91F_6) \\
F_0 &= F^0, \quad F_2 = \frac{1}{225}F^2, \quad F_4 = \frac{1}{1089}F^4, \quad F_6 = \frac{25}{184081}F^6
\end{aligned}
\tag{162}
$$

for the f^N configuration [4]. The term energies for d^N assume, to some extent, a simple form when expressed as functions of A, B and C. The E^j parameters (with $j = 0, 1, 2, 3$) for f^N

allow to decompose $\mathcal{H}_C$ into parts having well-defined properties under the action of the groups of the $SO(7) \supset G_2 \supset SO(3)$ chain.

As a last example, let us consider the parametrization defined by (159) with

$$b(\ell)_{\lambda k} = (-1)^{\lambda}(2\ell + 1) \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \ell & k & \ell \\ -\lambda & 0 & \lambda \end{pmatrix} \tag{163}$$

In this parametrization, the $\mathcal{H}_C$ operator can be rewritten as

$$\mathcal{H}_C = \sum_{\lambda = -l}^{l} V_{\lambda} \tag{164}$$

with

$$V_{\lambda} = \mathcal{E}^{\lambda} \sum_{k=0,2,\ldots,2\ell} (2k+1)b(\ell)_{\lambda k} \sum_{i<j} \left(\mathbf{u}^{(k)}(i) \cdot \mathbf{u}^{(k)}(j) \right) \tag{165}$$

We of course have $V_{\lambda} = V_{-\lambda}$ and therefore there are $\ell + 1$ independent components V_{λ} in $\mathcal{H}_C$. The $\mathcal{E}^{\lambda}$ parametrization was investigated in [139, 140, 141]. Let us simply mention that the part V_0 of $\mathcal{H}_C$ corresponds to a sum of surface delta interactions and that $\mathcal{H}_C$ can be reduced to V_0 for

$$F^k = (2k+1)F^0 \tag{166}$$

for $k = 0, 2, \ldots, 2\ell$. In the special case of the d^N configuration, it is to be realized that relation (166) corresponds to the Laporte-Platt degeneracies [142] (see also [9, 139, 143]) which occur for $B = 0$.

6 Closing remarks

Starting with the idea to substitute for the numerical methods of Slater, Condon and Shortley general methods close both to Dirac's ideas on quantum mechanics and to those of Wigner about the use of symmetries in physics, Racah developed practically in 20 years universal methods (irreducible tensor methods and group theoretical methods) used in many fields of physics and chemistry. In particular, the application of Racah's methods in atomic, nuclear and elementary particle physics as well as in group theory (Wigner-Racah algebra, state labeling problem) are well-known. We have shown how the use of Racah's methods in conjunction with $SU(2) \supset G^*$ or $SO(3) \supset G$ symmetry adapted bases and effective operators yields sophisticated models in crystal- and ligand-field theories. In last analysis, these models are fully described by chains of groups, viz., the $U(5) \supset SO(5) \supset SO(3) \supset G$ chain for the d^N configuration in G and the $U(7) \supset SO(7) \supset G_2 \supset SO(3) \supset G$ chain for the f^N configuration in G.

As an application of current interest in the present days, we have shown the importance of the chain $SO(3) \supset C_d$ for deriving a complete set of mutually unbiased bases when d is a prime integer. These bases are very useful in quantum information (quantum cryptography, quantum

state tomography, quantum error codes) and equally in quantum mechanics (discrete Wigner function, mean King problem, path integral formalism).

A common denominator to Sections 2, 3 and 4 is the notion of "chains of groups". Although chains of groups were in use before Racah (e.g., see the works by Ehlert on CH_4 [144], Bethe on crystal-field theory [29] and Wigner on supermultiplets of nuclei [145]), his contribution to that part of applied group theory is essential and represents one of its major achievements.[1] The interest for Physics and Chemistry of chains involving (noncompact and/or compact) continuous as well as finite groups is now well established. Such chains turn out to be useful in the investigation of broken symmetries which may arise either via descent in symmetry (Zeeman effect, homogeneous and inhomogeneous Stark effect, ligand-field effect, etc.) or via spontaneous symmetry breaking (Landau and Jahn-Teller effect, symmetry breaking in elementary particle physics, etc.). In Racah's approach, which excludes the cases of external or Lorentzian and internal or gauge (super)symmetries, one group of the chain is a high symmetry group corresponding to a zeroth order approximation (like the cubic group in ligand-field theory) and another one is a low symmetry group corresponding to a first order approximation (like the tetragonal or trigonal group in ligand-field theory). The two symmetry groups correspond to known or postulated symmetries depending on whether the nature of the interactions involved is known or unknown. According to Wigner's theorem [147], these symmetry or invariance groups (which leave invariant an Hamiltonian operator) provide representation labels or good quantum numbers for describing the state vectors. The other groups of the chain are dynamical or noninvariance groups in the sense that not all of their generators or elements commute with the Hamiltonian. They can describe part of the interactions and are generally introduced to make the chain as multiplicity-free as possible. Finally, the various groups of the chain are used to classify the state vectors and the (known or postulated) physical interactions. When elaborating a model based on symmetry considerations, the latter point is of considerable importance from a qualitative point of view (for level splitting and for selection rules) and a quantitative point of view (for the calculation of energy or mass matrices and transition probabilities). The preceding considerations apply to nuclear, atomic, molecular and condensed matter physics and also to quantum chemistry (chains of groups are even useful for classifying chemical elements [148, 149, 150]). Note that the situation is a bit different in elementary particle physics since the notion of classification groups (with the pioneer works by Heisenberg, Sakata, Gell-Mann, Ne'eman and Zweig going from the $SU(2)$ isospin group to the $SU(3) \supset SU(2)$ chain involved in the first quark model) evolved to gauge groups (going from the $SU(3) \otimes SU(2) \otimes U(1) \supset SU(3) \otimes U(1)$ standard model to the grand unified models based on the $E_8 \supset E_7 \supset E_6 \supset SO(10) \supset SU(5) \supset SU(3) \otimes SU(2) \otimes U(1) \supset SU(3) \otimes U(1)$). However, in any field of physics there is a common scheme, namely,

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[1]A fundamental result proved by Racah is that for a chain of groups having for head group a Lie group of order r and rank l, one can associate a complete set of commuting operators of cardinal $(r+l)/2$ (i.e., l Cartan operators plus l Casimir operators plus $(r-3l)/2$ labeling operators, some of the operators being Casimir, Cartan or labeling operators of the chain) [5]. See [146] for recent developments on this subject.

$$\text{(super)symmetries} \rightarrow \text{chain of groups} \rightarrow \text{invariance or}$$
$$\text{co-variance} \rightarrow \text{conservation laws or good quantum numbers.}$$

To close this paper, let us add some further comments. Racah founded the main school of theoretical physics in Israel. He had a strong impact on (national and international) committees and on various research groups in theoretical and experimental spectroscopy (including the Laboratoire Aimé Cotton in France).

Racah had many students who deeply contributed to atomic and nuclear spectroscopy; they are profusely quoted in the review by Zeldes [151]. We would like to complete the list of students in the bibliography of Zeldes with a few words about Moshé Flato (Tel Aviv 1937 - Paris 1998), a student of Racah during the period 1959-1963, who contributed to spread the ideas of Racah on crystal- and ligand-field theories. Flato achieved his M.Sc. thesis under the supervision of Racah in 1959 and prepared in 1960-1963 a Ph.D. thesis on a subject of nuclear physics (dealing with the $Sp(2n) \supset U(n)$ chain in connection with the Elliott-Flowers model) given by Racah.[2] When Flato came to France in 1963 his interest shifted to noncompact groups. He started working on Lorentzian symmetries and strong interactions when he was at Institute Henri Poincaré in Paris (1963-1964). After that he was Associate Professor of Physics for three years at Université de Lyon, then moved to Dijon in mathematics. Flato got in 1965 a Doctorat ès Sciences Physiques from Université de Paris on the basis of his works on elementary particle physics.[3] Flato pursued a brilliant career both in France and worldwide, dealing with a great variety of subjects in physics and in mathematics. Flato evolved from theoretical physics to mathematical physics and mathematics.[4] Among his many interests and contributions, let us mention the following: mass formulas (in relation with internal and external symmetries), conformal field theories; infinite-dimensional representations of Lie groups, singletons, AdS_4/CFT_3, composite electrodynamics; nonlinear representations of groups, covariant PDEs, global existence theorems for field theories (Yang-Mills, Maxwell-Dirac); and especially the role of deformations in physics, including the now 35 years old and still frontier area of deformation quantization (symplectic and Poisson

---

[2]According to Daniel Sternheimer, Flato was Racah's preferred student, probably the most brilliant in his generation. The families were friends since WWII when Flato's father was chief engineer of the British Mandate in Jerusalem. When Racah became Rector, he asked Flato to deliver (during 2 years, while Flato was doing military service) the traditional Racah lectures on group theory in physics, and recommended him for a course on solid state physics at Bar Ilan University, which Flato delivered without the compulsory yarmulke to students about his age.

[3]According to Sternheimer, after the death of Racah in 1965 (in Firenze on his way to join Flato in Paris) Flato decided not to publish the joint paper which they were preparing in nuclear physics. Racah had taken the manuscript with him in Firenze and intended to finalize it in Paris. Flato did not either defend in Jerusalem his Ph.D. based on that paper. Anyhow that became moot since he had already a French D.Sc.

[4]According to Sternheimer, his coworker for 35 years who heard with him a course on the theory of distributions by S. Agmon in Jerusalem in 1958-59, Flato had a dual training in physics and mathematics. Before opting for Racah he had considered working with S. Amitsur in algebra or with N. Rosen in relativity.

manifolds), quantum groups and noncommutative geometry. In 1968 Flato founded what was later called the Laboratoire Gevrey de Mathématique Physique at Université de Bourgogne and in 1975 Letters in Mathematical Physics and two series of books published by Reidel (Kluwer). He had numerous students in France and abroad and a strong impact on Society (IAMP, Marie Curie chairs, Scientific Council of UAP). For more details, see [152, 153].

Racah and Flato shared important scientific and human qualities. Both were excellent teachers and at the same time exceptional researchers with a good sense of the duality theory-experiment, convinced of the importance of symmetries in physics. They knew how to communicate enthusiasm, give the right impulse to their students and collaborators, and inspire them to solve problems. Both had a strong impact on scientific communities and on national and international committees and enterprises. We learned and can still learn many things from them both from the human and scientific points of view. Their impact will last for a long time. We shall not forget them.

Acknowledgements

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