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Giulio RACAH Centennial Conference

Rutwig Campoamor-Stursberg and Luis J. Boya (Editors)

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COMMUNICATIONS

Foreword

In the RACAH CENTENNIAL CONFERENCE, which took place from February 21-24, 2010 at the Paraninfo of the University of Zaragoza,[1] we intended to review the scientific contributions of G. Racah on the light of new developments in the last part of the XX century. Various expert speakers were invited to report on the actual status of the spectroscopy in its three branches, molecular, atomic and nuclear, and others were invited to cover the different aspects of the algebraic machinery introduced by Racah. Besides plenary speakers, several practitioners of Racahs techniques contributed presenting short communications. The event also covered Giulio Racahs scientific biography, as well as an overview of his influence in the creation and establishment of theoretical physics Institutes in Israel, in the historical context they occurred. This historical retrospective was presented by direct collaborators and disciples of G. Racah.

Unfortunately, due to some difficulties of different nature, some of the specialists originally intended in the programme, like B. R. Judd (Baltimore, USA), David Rowe (Toronto, Canada), Igal Talmi and Nissan Zeldes (Jerusalem, Israel) and Sigitas Alishauskas (Vilnius, Lithuania) could finally not attend the conference.

This meeting was possible thanks to the financial and infrastructure support of the following institutions:

- Fundación Ramón Areces, Madrid
- Diputación General de Aragón
- Universidad de Zaragoza
- Real Academia de Ciencias de Zaragoza

The organizers are indebted to R. Nuñez-Lagos for accepting to be the Scientific Secretary of the conference. We also extend our gratitude to J. F. Cariñena, M. Asorey, J. Clemente Gallardo, V. Azcoiti and H. de Guise for further support and help in some critical problems of last minute. Special thanks go to Esther Hernández Gimeno. Many organization aspects wouldn't have worked without her expertise and assistance.

Finally we would like to thank the following persons that accepted to intervene in the opening ceremony of the conference in representation of their institutions:

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[1] The official site of the meeting is `http://www.unizar.es/acz/congressRacah/`

- Julio Rodríguez-Villanueva as representative of the Scientific Board of the Fundación Ramón Areces.
- Anabel Elduque as the Dean of the Faculty of Sciences of the University of Zaragoza.
- José Antonio Mayoral in representation of the Rector of the University of Zaragoza.

The conference consisted of a limited number of one hour plenary talks, as well as a number of short communications (30 min.). The original plan of editing the proceedings including all the interventions finally had to be turned down. However, following the wishes of the organizers, we decided to edit at least a volume that could be seen as representative of the contents of the Racah Centennial Conference. At this point the special role played by prof. M. R. Kibler in the achievement of this objective has to be emphasized. Certainly, without his encouraging support these Proceedings would have never existed.

The Editors

Rutwig CAMPOAMOR-STURSBERG
Luis Joaquín BOYA

Plenary speakers

For completeness in the description of the conference, we enumerate the plenary speakers in the same order of intervention in the conference, and reproduce the abstract of the contribution they held.

Issachar Unna (Jerusalem): G. Racah: The Man and his Work

An introduction to the G. Racah Centennial Conference. Racah's life and his achievements will be presented. Special attention will be devoted to Racah's contributions to nuclear spectroscopy. Some results induced by and obtained with his methods by Igal Talmi and I. Unna will be presented.

Shmuel Elitzur (Jerusalem): Racah Algebra and 2D CFT

The Racah coefficients and their relations were initially formalized for the study of atomic spectra. In the late eighties theoretical interest in 2 dimensional Conformal Field Theories was intensified mainly in connection to string theory. It turned out that the Racah formalism was relevant in this field. The role of Racah's algebra in this context will be reviewed.

Gerardo Delgado Barrio (Madrid): Microscopic Superfluidity in Helium Clusters

Spectroscopic studies of simple molecules surrounded by He atoms show a drastic difference depending on the fermionic or bosonic character of the solvent atoms. A quantum chemistry-like approach has been recently developed in our group to deal with HeN -BC doped helium clusters, where the BC dopant is a conventional di-atomic molecule. The central idea is to consider the He atoms as "electrons" while the B and C atoms play the role of the nuclei in standard electronic structure calculations. The procedure provides spectral simulations and, hence, making feasible to do proper comparisons with current experiments. However, due to the big difference of masses of He and electrons, and also to the replacement of Coulomb potentials by molecular interactions, it is worthy to asses at what extent the approximations involved (decoupling of orbital angular momenta of the He atoms from the BC rotation and adiabaticity of the BC stretch versus de He motions) lead to accurate results. Here, we consider several diatomic molecules as dopants. The model provides the energy levels of the cluster and the intensities of the main lines of the spectrum at low temperatures.

Piet Van Isacker (Caen): Seniority in Quantum Many-Body Systems

In 1943 Racah introduced the seniority quantum number in the classification of electrons in an l^N configuration where it appears as a label additional to the total orbital angular momentum L and the total spin S. About ten years after its introduction in atomic physics, seniority was adopted in nuclear physics for the jj-coupling classification of nucleons in a single-j shell. Seniority refers to the number of particles that are not in pairs coupled to angular momentum $J = 0$. In nuclear physics this concept has proven extremely useful, especially in semi-magic nuclei where only one type of nucleon (neutron or proton) is active and where seniority turns out to be conserved to a good approximation.

In this talk a review is given of the use of the seniority quantum number in many-body systems. The necessary and/or sufficient conditions for seniority conservation in a system of identical bosons or fermions (known since long) are briefly recalled. More recently, the possibility of partial seniority conservation has been pointed out when most states are mixed in seniority but some remain pure. An application of these ideas to the occurrence of nuclear isomers is presented. Seniority isomers are nuclear states characterized by electromagnetic decay hindered by selection rules related to the seniority quantum number. A simple analysis is presented of their possible formation with reference to the nickel isotopes $^{70-76}$Ni and the $N = 50$ isotones from molybdenum to cadmium. It is shown that the existence of seniority isomers is predominantly governed by the quadrupole pairing matrix element of the nucleon-nucleon interaction.

Francesco Iachello (Yale): Spectrum Generating Algebras and Superalgebras

Algebraic theory, that is, the mapping of all physical operators onto the elements of a Lie algebra $\mathfrak{g}$, will be briefly reviewed. Applications to spectroscopy of atomic nuclei (Interacting Boson Model with algebra $\mathfrak{g} \equiv U(6)$) and to the spectroscopy of molecules (Vibron Model with algebra $\mathfrak{g} \equiv U(4)$) will be presented. The dynamic symmetries of these models, corresponding to the breaking of the algebra $\mathfrak{g}$ into its subalgebras will be discussed.

In recent years, algebraic theory has been extended to describe mixed systems of bosons and fermions by mapping the operators onto the elements of a graded Lie algebra $\mathfrak{g}^*$. Applications to atomic nuclei (Interacting Boson-Fermion Model with algebra $\mathfrak{g}^* \equiv U(6/\Omega)$) will be presented. The dynamic supersymmetries of these models, corresponding to the breaking of $\mathfrak{g}^*$ into its graded (or not) subalgebras will be discussed and experimental examples presented. This is the only case known in Nature so far of supersymmetry.
Algebraic theory makes use of methods and techniques developed by Giulio Racah on the 1940's and summarized in his lecture notes at Princeton University "Group Theory and Spectroscopy".

Maurice Kibler (Lyon): Impact of G. Racah in Crystal Field Theory

The first part of this talk deals with the impact of the methods of Racah in crystal- and ligand-field theories (two theories for explaining the electronic and magnetic properties of partly-filled shell ions in molecular, solid-state or biological environments). Emphasis is put on developments (during the period 1959-1995) for the calculation of (i) the energy levels for an ℓ^N ion embedded in an environment described by a point group G and (ii) the intensities of one- and two-photon transitions between the levels. The second part of the talk is devoted to some by-products as (i) the Wigner-Racah algebra of the group $SU(2)$ in a nonstandard basis $SU(2) \supset G^*$ (with $G \sim G^*/Z_2$), the Wigner-Racah algebra of a subgroup G^* of $SU(2)$, and (iii) the derivation of mutually unbiased bases in quantum information.

Luis Egido (Madrid): Recent developments in Nuclear Structure Physics

The availability of intense radioactive ion beams as well as the development of new instrumentation with increased efficiency and resolution (4π γ-ray spectrometer, recoil separators, particle detectors, etc.) led to a revival of the field of nuclear structure physics during the last decades. New phenomena and surprising nuclear properties have been discovered, such as neutron halos and skins, the disappearance of well-established and the nascency of new magic numbers far-off stability, new radioactive decay modes, etc., which enforced a modification and extension of our view of the atomic nucleus.

Scientific communications

Besides the plenary talks, various other contributions were presented at the conference. We also enumerate them with abstract in the order they were placed in the programme.

Fernando Bartolomé (Zaragoza): Racah Algebra and Sum Rules in magnetism in Solids

The basic theoretical principles of atomic spectra were published in 1935 by Condon and Shortley in the classic book "The Theory of Atomic Spectra". The group-theoretical methods of Giulio Racah, presented in the series of four classic Physical Review papers "Theory of Complex Spectra" enabled the application of atomic theory to systems of broad interest. In particular, the multiplet calculations, allowed by the implementation of Racah and Judd's methods into a workable code for radiative transitions by Bob Cowan in the sixties, have enabled the understanding of complicated core level spectra of transition metal, rare earths and actinide compounds, including x-ray absorption, photoelectron emission, and Auger spectroscopies, among others. The magnetism of compounds and molecules containing 3d and 4f ions was also understood, at least qualitatively, by "crystal field" calculations. In parallel, the Racah methods and the "Cowan code" paved the way to the extremely fruitful Theory of Simple Spectra by Theo Thole: the study of the integrals instead of the details of the x-ray absorption spectral lines allowed the study of branching ratii and the stablishment of the so-called sum rules by Theo Thole and Paolo Carra. The sum rules allow the separate determination of orbital and spinorial magnetic moments. The talk will review the impact of the sum rules in modern magnetism of solids, and some future trends will be discussed, including developments in nanomagnetism, electron microscopy and quantum phenomena.

Joaquín Sánchez-Guillén (Santiago de Compostela): Abelian Ideals and Infinite Conservation Laws

In the generalization of the zero curvarture integrability to any dimension by the author with Alvarez and Ferreira, we show how the flatness follows generally when the relevant d-1 dimensional antisimetric tensor takes values in an abelian ideal of a Lie algebra and it is covariantly constant. When these conditions are the equations of motion of a field theory, the representations of the nonsemisimple algebra provide ifinite conserved currents given by the adjoint action , which also have a continuum expression with interesting geometrical properties. Relevant applications for sigma and Skyrme type models are given.

Juan Mateos (Salamanca): Supersymmetric Quantum Mechanics of Integrable Systems

In standard supersymmetric quantum mechanics the Hamiltonian factorizes as the anticommutator of the supercharge and its adjoint. Search for the spectrum of energy eigenfunctions is accordingly very easy in SUSY quantum mechanical systems of one degree of freedom. If there are more than one degree of freedom usually factorization is not enough to find analytically the spectrum. I will describe how to deal with the spectra of SUSY extensions of integrable systems. In particular, I plan to present SUSY extensions of the Kepler, the Euler two Newtonian centers, and the Neumann problems.

Luis Joaquín Boya (Zaragoza):

We frame the definitions of $3j$, $6j$ and $9j$ (Racah-Wigner) symbols for arbitrary tensor products of irreducible representations of compact (mainly simply reducible) groups. Some interesting facts on their properties are discussed.

Mariano del Olmo (Valladolid): q-Coherent States of the Harmonic Oscillator

The time-evolution of the quantized version of the harmonic oscillator obtained through a q-dependent family of coherent states is studied. The semi- classical phase trajectories present interesting features when 1/q is a quadratic Pisot number.

Maria Luisa Sarsa (Zaragoza): Nuclear and Particle Physics at the Canfranc Underground Facility

Underground facilities around the world are devoted to very sensitive experiments impossible at surface level laboratories. The main lines of research are: neutrino physics, direct search for dark matter, nuclear astrophysics and very rare decays (as proton decay) but also new and interesting topics are coming into scene, life under extreme conditions and geological studies are some examples. The Canfranc Underground Laboratory has a 25 years experience in underground physics: starting as two small 10 m^2 labs has recently become one of the few Spanish ICTS (scientific and technological singular facility). Previous efforts in the search for the neutrinoless double beta decay and the galactic dark matter carried out at Canfranc will be reported as well as current experiments and prospects for the future. In between, the relevance of the studied topics in the frame of the Nuclear and Particle Physics will be stated.

Hubert de Guise (Lakehead): $\mathfrak{su}(1,1)$ Intelligent States: Construction and Squeezing

In this contribution I will show how the basic intelligent states of the algebra $\mathfrak{su}(1,1)$ can be easily constructed for the $k = 1/4$ and $k = 3/4$ representations. Two such realizations are then combined to obtain intelligent states for higher k irreps: it will be shown in particular how an $\mathfrak{su}(1,1)$ intelligent state can, for an arbitrary realization, be constructed by combining a “squeezed” vacuum with an appropriately prepared superposition of Fock number states. A simple application to squeezing of $\mathfrak{su}(1,1)$ observables will be discussed, illustrating some unorthodox properties of $\mathfrak{su}(1,1)$ squeezing and the difficulties in properly defining this concept in $su(1,1)$. In particular it will be shown that $\mathfrak{su}(1,1)$ squeezing can occur in single-particle $\mathfrak{su}(1,1)$ representations ($k = 1/4$ or $k = 3/4$), thus suggesting that squeezing is not necessarily due to multi-particle quantum correlations.

Mariano Santander (Valladolid): Division Algebras, Composition Algebras and Triality

Division algebras are alternative $*$-algebras over the reals admitting a positive definite quadratic form with the composition multiplicative property. There are only four such algebras ($\mathbb{R}$, $\mathbb{C}$, $\mathbb{H}$, $\mathbb{O}$). The octonion algebra, the eccentric member of the family, displays further a surprising triality, which is apparently an specifically octonionic property. Among other things, this triality is somehow behind some of the known constructions of the exceptional Lie algebras out of the octonions.

Triality is however not a specific property of octonions; instead it rests on alternativity and on the composition property; thus the essential token in the triality is not 'to be octonionic' but to be 'composition alternative $*$-algebra'. Here we discuss in gore detail this question, reaching triality in a direct and constructive way for all composition alternative $*$-algebras over the reals. In addition to $\mathbb{R}$, $\mathbb{C}$, $\mathbb{H}$, $\mathbb{O}$, these algebras include only the split variants of complex, quaternions and octonions, denoted ($\mathbb{C}'$, $\mathbb{H}'$, $\mathbb{O}'$) and we discuss for all these the structure of several Lie algebras related with these alternative composition algebras.

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Figure 1.— Photograph of the participants at the front of the Paraninfo.

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GIULIO RACAH: THE MAN AND HIS WORK

ISSACHAR UNNA

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Abstract

An introduction to the Giulio Racah Centennial Conference. Racah's life and his achievements will be presented. Special attention will be devoted to Racah's contributions to nuclear spectroscopy. Some results induced by and obtained with his methods by I. Talmi and I. Unna will be presented.

This conference celebrates the centennial of Giulio Racah. I am very honored and have the great pleasure to thank the organizers of this conference in this wonderful place. In particular, I want to thank Professor Luis J. Boya and the RAMON ARECES FOUNDATION. By the way, Prof. Boya and I are also celebrating the Jubilee of our first meeting in another beautiful place. In Varenna, 1960, the International summer school "Enrico Fermi" was devoted to "Nuclear Spectroscopy". Racah was the "Direttore del Corso", Nissan Zeldes was the "Secretario Scientifico". Racah gave the course on "Mathematical Techniques", since, as he said in his opening words, "I am more familiar with the mathematics than with the physics of nuclear spectroscopy". My Thesis adviser and Racah's devoted pupil, Igal Talmi, gave "The Nuclear Shell Model". Igal celebrated now his 85th birthday, full of vigour and activity. Unfortunately, he could not come today because he is the organizer of a conference at the Weizmann Institute at exactly the same dates.

The opening of the Hebrew University took place in 1925. At about the same time Quantum Mechanics was born.

For fifteen years, since its opening, the Hebrew University was desperately looking for a good theoretical physicist who was ready to teach and do research in it. Albert Einstein was consulted on an almost daily basis. Several giants were seriously approached and on the verge of agreements, like George Placzek, Felix Bloch, Fritz London and Eugene Wigner. All these efforts failed.

All these fifteen years Quantum Mechanics, with all its successes, was completely impotent in dealing with atoms having more than 2 active electrons, which meant that most atomic spectra could not be explained with the new theory.

Then appeared Racah, a bright young physicist (age 30) from Italy, full of theoretical vigour, and a determined Zionist, and filled the empty position at the Hebrew University as well as the existing void in Quantum Mechanics, like the last missing piece in a jigsaw puzzle completing the picture in all directions. Racah arrived at the Hebrew University in 1940 (after the outbreak of WWII). He had excellent reference letters by his beloved teacher, Enrico Fermi, and also by Wolfgang Pauli, Niels Bohr, Kramers and Fritz London. Fermi wrote:

"Of the cadidates you mentioned I can provide information only on Prof. Racah. I knew him very well... he worked with me for some time in Rome. I could therefore appreciate [his] really outstanding knowledge of physics, and follow very closely his interest in scientific work. His contributions to the quantum theory of radiation are particularly valuable. I have to mention that he arrived independently and almost simultaneously with Bethe and Heitler at the same results concerning the emission of radiation by high-energy electrons. May I be allowed to add, that in my opinion Racah possesses all the personal attributes to lead most effectively young students in scientific work."

(Fermi, 8 September 1939)

In 1951 Racah writes from Princeton to the rector of the Hebrew University:

"I went to visit my Rebbe - Fermi. I did not write so far because I was busy with discussions (and small talk). After all, these were the main purpose of my trip. Doing work I can much better at home in Jerusalem, at least late at night when there are no committee meetings..."

(Racah, 29 January 1951)

Pauli wrote:

"I know him personally, and know his works well. An extraordinary mathematical talent, and in perfect command in any problems and methods of modern theoretical physics (wave mechanics and quantum electrodynamics) .... He succeeded in solving problems which deterred others (the creation of pairs as a result of the collision of fast charged particles with atoms, and also the computation of the radiation of very fast particles ...) problems which are at the core of the most modern theories of cosmic rays . . . and therefore he is qualified also to cooperate with an experimental research institute. He is also extraordinarily conversant with questions of principle .... In conclusion, I do not know a candidate more suitable for a professorship in theoretical physics in Jerusalem than Prof. Racah. As regards [Reinhold] Furth (Prague) [who also was under consideration], he is undoubtedly a good craftsman particularly in the area of Brownian motion, but he is less original, and of weaker attitude to modern physics."

When Racah arrived in Jerusalem in 1940 he had to cope with a new country, new culture, new language, and with complete scientific isolation. Yet, he called the year 1940 "The best year of my life". During this year he learned perfect Hebrew [but even speaking Hebrew he never lost his heavy musical Florentine accent], he married his loving girl Zmira Mani, daughter of a well rooted Jewish-Palestinian family and he wrote his first paper, of the famous four, on the "Theory of Complex Spectra".

The work on these papers was accomplished in complete seclusion from the scientific world. And these papers made his fame. They contain what is now known as the "Racah Algebra". The second paper was included in the "Physical Review Centennial Volume" (1995), which contains the 200 most important articles in a hundred years. Racah's papers were also on the short list of the most cited papers in the 1950s. Hans Bethe in a review of the centennial volume writes:

"The paper by Giulio Racah ["Theory of Complex Spectra"] gives everything the theorist needs to work on the subject."

The content of these papers is now part and parcel of every advanced textbook in Quantum Theory. Racah was a prominent figure, very dynamic and full of vigour. Each of his classes, or even an eventual conversation in the corridor (never gossip or nonesense) was an unforgettable experience. He was an excellent teacher. I had the great privilege to aquire the whole base of physics – classic and modern – from him in his courses. Beginning with classical mechanics and electrodynamics, ending with QED, atomic spectroscopy and nuclear physics. The most devoted pupil and assistant of Racah was Nissan Zeldes, who was invited to give this talk, but was, unfotunately, unable to come. He published recently a big article in the "Archive for the History of Exact Sciences" [63, 289-323, (2009)]: "Giulio Racah and Theoretical Physics in Jerusalem" [I helped with the final editing of it]. Another relevant reference is my paper in "Physics in Perspective" [2, 336-380, (2000)] : "The Genesis of Physics at the Hebrew University of Jerusalem".

My thesis advisers were Igal Talmi and the late Amos de-Shalit, his world known pupils. But they were at the Weizmann Institute, Rehovoth, and I was still studying in Jerusalem. So I went to get advise from Racah whenever I got stuck with my calculations in nuclear shell theory. Later I learned that my questions motivated Racah to further developments of his theory in nuclear spectroscopy.

I shall not forget our excitement as students before each of his lectures. We were fighting for good seats in the lecture hall. Indeed, the lectures were masterpieces of clarity in content and presentation. With typical stubbornness he insisted on carrying out each calculation from start all through to the final results. The complicated expressions were written in perfect order, line after line, on the big blackboard. It could be the form of a hanging chain in classical mechanics, the detailed solution of a differential equation in quantum mechanics or calculating the refraction coefficients of light directly from Maxwell's equations. He did not omit any stage of the calculation. It was never "it easy to see" or "you can easily verify"

When he published his book together with his cousin Hugo Fano, "Irreducible Tensorial Sets", he told me that he and Fano had lots of fights over the book. I asked him why. He answered that "The reason was that we had a common grandmother who was very stubborn"

Indeed, stubbornness was a typical virtue of Racah, in the good sense of it. When he decided to carry out a calculation - nothing could stop him, even if it turned out to be very lengthy and extremely complicated. That is how he succeeded in calculating his coefficients and developing his algebra during long lonely nights.

Racah was a good friend with us, students, and showed his friendliness in so many ways. I remember, in particular, traveling with him, in his car from Jerusalem to seminars in Rehovoth. He invited us to join him and we felt honored and excited. During the trip we had lengthy talks, usually on scientific subjects. When he got excited during a discussion he would talk with both his hands in the air, and we trembled till his hands returned to hold the steering wheel. He showed high involvement in our students' life. He joined us in parties and volunteered with us in going to the country to build fortifications around isolated settlements. He arrived in a labourer's shirt, shorts and a big sun hat and was amongst the best workers out there. From time to time we could hear talks on better angular momenta coupling modes or new checks of matrix diagonalization programs coming out from one of the deep ditches, accompanied by the sounds of digging ploughs and spades.

A few years before his untimely death he had a car accident on his way to Eilath. Talking about it, he said he has an accident once every 20 years. He is glad he survived this one unhurt. Next time he will be old so he has nothing to be afraid of. It seems, this was his greatest mistake. At the age of 56 an accident of a different kind took his life when he was still full of vigour and abounding with plans.

Five years after his death the "Racah Institute of Physics" was established at the Hebrew University. In the same year a crater on the moon was officially named after him. In 1993 the State of Israel issued a post stamp with his portrait. Streets in Jerusalem and Beer-Sheva carry his name.

Racah is also remembered for many public activities at the Hebrew University,as well as nation-wide and international. Let me mention a few. He was member of commissions on standards and spectra by the International Astronomical Union, and IUPAP (later also IUPAC). The Joint Commission for Spectroscopy set Jerusalem as the clearing house for angular wave functions, giving all the information on the related calculations carried out worldwide so as to prevent overlapping activities. Thus, the theoretical physics department in Jerusalem became a world center for atomic spectroscopy. In his last years (1961-1965) Racah served as Rector and President of the Hebrew University. In this position he promoted the teaching of courses for students from African and Asian countries. He had the privilege to convocate a honorary degree on Haim Weizmann, the big Zionist leader, founder of the Hebrew University and the first Peresident of the State of Israel. Later he honored Felix Bloch with the Honorary Degree of the University.

He was amongst the founders of the Israel Academy of Sciences (1959). He served as member of the Scientific Council to the Prime Minister (later - the National Counsil for Research and Development) and was a member of Israel's Atomic Energy Commission. As such, he served as delegate to the Geneva International Conferences on the peaceful uses of atomic energy.

In 1961 he was convocated Doctor Honoris of Manchester University. The ceremony took place at the Rutherford Jubilee International Conference (celebrating 50 years to Rutherford's discovery).

I was fortunate to attend it. Many of the greatest physicists were there. Niels Bohr, Dirac, Peierls, Aage Bohr, Mottelson etc. I remember Niels Bohr, dressed with big blue garter of the "Order of the Elephant" dancing at the evening party. Racah received many honors and prizes during his academic life including the prestigious Israel Prize.

As mentioned, Racah applied most of his mathematical methods to atomic spectra. He felt that there were not enough nuclear spectroscopic data available for reliable calculations. But his interest and theoretical ideas were gradually shifting to the nuclear regime. The establishment of the nuclear shell model was a crucial step and motivated his ideas. His students Zeldes, de-Shalit, Talmi and others took over the torch into the nuclear spectroscopy. Zeldes specialized in nuclear masses. He and the others took shell model calculations to their real great sucesses. This was the time when I entered the scene (1958).

In the year 1944 Racah gave the major talk at the Israel Chemists Organisation. The title was: "Introduction to Nuclear Theory". At the end of his talk he said: " If it is true that new neutrons are emitted upon the explosion of Uranium induced by neutrons then we might obtain a chain reaction. If this was achieved I do not know, since from the beginning of the war this kind of information is kept secret" . He then spoke about the difference between slow and fast neutrons and the possible necessity of separating the U235 component. "But", he ended, "we shall have to wait till the end of the war to know where the nuclear science stands."

On the 18th December 1945 he gave again a talk at the same forum: "New Developments in Nuclear Theory". This talk was post Hiroshima and it dealt with the new knowledge attained ("although, a lot is still kept secret", as he said). Ten years later I attended the course on Nuclear Theory given by Racah for a whole semester. But his mathematical methods I learned in his course on Atomic Spectroscopy as well as by attending his seminar on Selected Topics in Atomic Spectroscopy. Here I discovered how much we can achieve in analysing spectra without making detailed assumptions on the form of the interaction. Actually, this is exactly what the Racah Algebra helps us do. In his atomic calculations the few Radial integrals are kept as parameters and the quantum predictions are made purely by applying Racah's algebraic and group theoretic methods to the angular parts of the wave functions.

These methods become even more important in nuclear spectroscopy where the basic interaction is unknown a priori. The assumptions we make in our caculations are minimal. All we assume is that the nuclear interaction is a two body interaction, and that it does not change with the addition of nucleons so long as we are confined to a single nuclear shell. Thus, we could use the two particle spectra, applying Racah's methods to calculate the spectra of n particles in the same open shell.

Some of Racah's inventions for efficient atomic calculations are even more spectacular in the nuclear context. In paticular, the concept of the seniority quantum number and the use of sophisticated Lie groups for the analysis of nuclear spectra. The seniority is first introduced in his TCS III paper (1943). Explicit use of group theory appears first in TCS IV (1949), where Racah caculated f^n configurations. In this paper he also proves a very useful lemma. A much more systematic exposition of Lie groups and their application to spectroscopy was given in a set of lectures delivered in 1951 at the Institute for Advanced Study in Princeton. [here, Racah also met Albert Einstein for the first time.]. These important lectures were written as notes by Eugen Merzbacher and David Pank. For years these notes were so hard to get that they almost became collectors' items. Ten years later, by a lucky chance, a copy was uncovered in CERN. With Racah's permission they mimeographed it for the benefit of a wider audience. Later the notes appeared as a book in the Springer Lecture Notes series.

In a small and quite unknown paper [L.Farkas Memorial Volume, Research Council of Israel, 1, 294-304 (1952)] Racah transferes his methods specifically to nuclear jj-coupling spectra. Here, as it turns out one has to use the Symplectic group instead of the Orthogonal group. This group was first introduced by Herman Weyl in his Classical Groups (Princeton, 1938). This group leaves a skew- symmetric bilinear form invariant. This is necessary because the scalar two-body wave function, the $j^2 \quad (J=0)$ is antisymmetric contrary to the $l^2 \quad (L=0)$ case. This group gave a very efficient tool in calculating j^n spectra. We (Igal Talmi and myself) were able to obtain some excellent fits with experimental data. The first good case was the binding energies of nuclei with $1f_{7/2^n}$ configurations (neutrons or protons) [I. Talmi, Phys. Rev. 107, 326 (1957)]. Even more exciting was a result we obtained for ^{11}Be. Using the the simplest Racah methods we confirmed its positive parity ground state, which was contrary to what everyone believed [I. Talmi and I. Unna, Phys. Rev. Letters, 4, 469 (1960)]. In spite of its apparent simplicity, this was an exact shell model calculation. Good reviews of the methods and of our results can be found in: I. Talmi and I. Unna, Annual Rev. Nuclear Sci., 10, 353 (1960) and I. Talmi, Revs. Mod. Phys., 34, 704 (1962). The latter summarizes many of my early works on nuclear spectroscopy.

Later, I did some basic work on applying BCS , RPA, second RPA and HF to nuclei and dealing with the eliminations of spurious states [see, for example, Spectroscopic and Group Theoretical Methods in Physics, Racah Memorial Volume, edited by F.Bloch / S. G. Cohen / A. De-Shalit / S. Sambursky / I. Talmi (Notrth Holland 1968), p. 403]. Now, I do history – mainly working with the huge editorial project of editing the writings of Einstein, the EPP, Caltech, Pasadena, and, believe me, working on Einstein's correspondence and unpublished material we make a lot of exciting discoveries.

Thank you!.

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ON GIULIO RACAH

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Giulio RACAH (Firenze, Italy, 9-II-1909; Firenze, 28-VIII-1965) was a remarkable italo-israeli theoretical physicist. He graduated in Physics in Firenze in 1930, studied after under Enrico Fermi in Roma, being nominated Professor of Physics in Pisa in 1937. But in 1939, due to the racial laws imposed upon Mussolini by Hitler, he had to emigrate to Palestine, at the time under British mandate, but after 1948 the actual state of Israel (Fermi himself, after receiving the Noble Prize, settled in the United States).

In Jerusalem he was professor of physics, and eventually Dean of the Faculty of Science and later became Rector of the Hebrew University (founded in the 1920s, Albert Einstein himself was involved in the creation), and acting President. He was instrumental in converting the Hebrew University in a first class institution for modern science, as it is still today.

Giulio Racah was rather active politically, and fought very much for the cause of Israel state: from 1942 until 1948 he belonged to the Haganah (Defense), a paramilitary organization which was instrumental in abolishing the British mandate and establishing the actual state of Israel en 1948. Racah also participated as a soldier in the 1948 and 1956 wars against the arabs. He did frequent visits to the US, and in several of them he stayed at Princeton.

In 1958 he received the Israel Prize in exact sciences for his ever-lasting contributions to Physics, mainly in the domain of atomic and nuclear spectroscopy. In 1965, in a trip from Jerusalem to Amsterdam, he stopped in his family home in Firenze and unfortunately died in a domestic gas-escape accident.

The great transcendence of his research was the clarification of complex atomic spectra, for what he developed some techniques which are used very much even today; he started first with “open shell” atoms (incompletely filled last electronic shell in complex atoms, starting with 3d (Fe) row): the techniques that Racah introduced to study these complex atomic spectra are standard today. Then, he was the first to attack the very complex spectroscopy of lanthanides, those atoms with the 4f shell filling (14 elements). His four papers in Physical Review, covering the period 1942-49 are landmarks: they are reproduced, for example, in the Reprint volume by Biederharn [1]. In a way, the so-called “Racah algebra” is a continuation of the Wigner coefficients (ca. 1930) to combine angular momenta. Group theory was first employed in Quantum Mechanics by H. Weyl and E.P. Wigner in the “heroic” period around 1926. Three books (a third one by B. L. van der Waerden) testify this, and run through several editions.

Racah introduced also generalizations like “coefficients of fractional parentage”, the seniority quantum number (vethek), very much used ever after both in atomic and in nuclear spectroscopy. In 1960, the Italian Physical Society, which organized annual summer schools in Varenna (in the shores of the Como lake), organized a course: Racah was the director of the summer course on ”Nuclear Spectroscopy”, in June, 1960 (that I attended), and I still remember his lectures, with a strong German accent, by Racah himself: “neutrons” he pronounced “noitrons”, similar to German; the proceedings were published by the Italian Physical Society [2]. Racah was settling the with his whole family, including his beautiful daughter Erella, who unfortunately also died pretty young.

His spectroscopic techniques were later published as a book which became a classic, entitled Irreducible Tensorial Sets, with his collaborator Ugo Fano [3].

In 1952 G. Racah gave some lectures on Lie groups in Princeton, published later as a CERN yellow report [4]: it is a fact that these lectures introduced the average theoretical physicist to the importance of Lie group theory for physics. When in the following decade (60) Murray Gell-Mann developed the SU(3)-flavour model group for strong interactions, physicist were convinced that a knowledge of this particular branch of modern mathematics have to be included in the curricula of the average theoretical physicist... and that is the case nowadays... Historically these studies were preceded by the very important work of E. P. Wigner (1939) on the unitary representations of the Poincar group to classify the elementary quantum system (elementary particles), which to day it is incorporated as a first chapter on books on Quantum Field Theory (e.g. S. Schweber [5], S. Weinberg [6], etc.).

The scientific contributions of G. Racah were not exhausted with spectroscopy; back in the 30s, working with the group of Enrico Fermi in Rome, Racah also made contributions to the operator C, for Charge conjugation (particle-antiparticle) ... in relation with spinors and in general fermions. In the fifties, Schwinger, Pauli, Lüders and others applied the results of Racah to prove the all-important “CPT” theorem, which says: from the continuous Lorentz invariance (Poincaré invariance, really), with locality and other plausible assumptions, one has CPT invariance, predicting particle-antiparticle would have equal masses and lifetimes; this has been checked so far successfully many times (see, e.g., the Tables of Particle Properties, published in Phys. Rev. and in Phys. Lett. every two years [7]). Racah also attempted to understand renormalization in a paper of 1946, which however was somewhat controversial.

Perhaps the most ever-lasting contribution of G. Racah to physics was the foundation of the Israeli school of Theoretical Physics, still flourishing today, with people like H. Lipkin, U. Fano, I. Talmi, Issachar Unna and others. One of most brilliant successors is Nathan Seiberg, actually

Professor in Tel Aviv University, which with E. Witten has revolutionized string theory. Today, the department of Physics of the Hebrew University holds the Racah Institute for Theoretical Physics.

To celebrate the Centenary of his birth in 1909, several Conferences were organized. We refer here only to two of them. In February 22-24, 2010, The "Academia de Ciencias de Zaragoza" sponsored one, with Luis J. Boya (University of Zaragoza) and Rutwig Campoamor-Stursberg (U. Complutense, Madrid) as organizers; we had the support of the "Fundación Ramón Areces" from Madrid. Among the foreign invited people we cite: I. Unna and S. Elitzur from Jerusalem, the latter being now the Director of the Racah Institute in the Hebrew University; P. van Isacker from the GANIL in Caen, France, M. Kibler from Lyon, France, F. Iachello from Yale University, USA, and H. de Guise from Lakehead, Canada. The cited "Academia de Ciencias de Zaragoza" is currently processing the Proceedings.

A second Conference was organized by the Hebrew University, Jerusalem itself, in June 6-8, 2010, under the title " Symmetry in Physics Research", and it took place in the "Maison de France" on the Safra Campus at Givat Ram, Jerusalem; LJB participated also in this Workshop; among the notorious speakers we must mention F. Iachello, I. Unna, again, N. Zeldes, Nathan Seiberg, Alain Aspect, etc. Also, a joint meeting in the Literary University at Mount Sion took place, attended by some of Racah's sons, and it was very profitable.

References

[1] L. Biedenharn and J. D. Louck "Quantum Theory of Angular Momentum" (Benjamin, NY 1965)

[2] Proceedings of the Course; in Varenna, Italy, "Nuclear Spectroscopy", 1960. Academic Press.

[3] G. Racah and U. Fani "Irreducible Tensorial Sets" (Academic Press, NY 1959)

[4] G. Racah. "Group Theory and Spectroscopy, Princeton Lectures 1952. Published as CERN "Yellow Reports".

[5] S. S. Schweber "Introduction to Relativistic Quantum Field Theory" (Harper and Row, NY 1961)

[6] S. Weinberg "Introduction to the Quantum Theory of Fields (Cambridge University Press, Cambride 1995)

[7] Review of Particle Properties. Physical Review and Physics Letters, Bi-annual publication.

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GIULIO RACAH, SPECTROSCOPY AND GROUP THEORETICAL METHODS IN PHYSICS

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The scientific influence of G. Racah can hardly be summarized in a few pages, as his methods and ideas dominate largely many of the modern techniques used in physics, notably those used in atomic and nuclear spectroscopy. This influence goes far beyond Racah's own publications (see list at the end of this article), as follows from the huge number of contributions of his students, collaborators and contemporary physicists outside the Hebrew University of Jerusalem. Although primarily associated to the algebra of tensor operators, an essential technique in theoretical physics, the ideas and methods of Racah are found in many different contexts, from the different branches of spectroscopy to labelling problems, classification schemes and crystal structures.[1]

The year 1949 can be considered as the origin of the modern application of Lie groups to the atomic shell theory, with the publication of the fourth seminal paper of Racah's series on complex spectra (papers 27, 30, 32, 35). The novelty of his approach was to introduce non-invariance Lie groups, in contrast to the usual symmetry groups used earlier and underlying the theory (specifically the rotation group $SO(3)$ in atomic spectroscopy).[2] The ansatz of Racah was also the first step towards a reconciliation of two opposed schools: the group theory defendants like Hermann Weyl (with his famous but opaque book "Gruppentheorie und Quantenmechanik") and the opponents of such methods, notably represented by Condon and Shortley with their important book "The Theory of Atomic Spectra".[3] Possibly this decline of interest concerning

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[1] An extensive review on Racah's impact in crystal- and ligand-field theories written by Prof. M. R. Kibler can be found in this volume.

[2] Even if E. Wigner can be credited to be the first having recognized the value of labelling problems with his supermultiplet model $SU(4) \supset SU(2) \times SU(2)$ of 1937, this approach was not fully accepted until much later.

[3] It is however remarkable that in this book, the authors made implicitly use of group theory when chosing adequate linear combinations of Slater determinants that actually corresponded to irreducible

atomic spectroscopy (and basic research in it) in the late 30's was influenced by the increasing attention devoted to the structure of nuclei following the Hahn-Straßmann fission experiments [1], as well as the exigences of wartime for their immediate applications [2].

For a certain time after 1949, many of Racah's results remained unnoticed in atomic spectroscopy, although their importance in nuclear physics was rapidly recognized and applied to specific situations. With Racah's technique, to just mention an example, H. A. Jahn enumerated the orbital states arising from the filling of the nuclear d-shell in the Russel-Saunders coupling, obtaining a classification of the states according to the rotation group $SO(5)$.[4].

Racah's work prior to his emigration to Palestine in 1939 is mainly focused on various problems of convergence of the self-energy of the electron, where he developed various methods that generalize the work of Majorana on elementary particles and antiparticles (refs. 1-4, 12-20, 22, 25, 26). He also devoted various articles to the hyperfine structure (refs. 5-8) following Dirac's theory of the electron. Special mention deserves reference 8, where the analysis of the hyperfine structure of Thallium and Mercury led to the observation of a structure arising from a displacement of the atomic levels in different isotopes. This phenomenon would become a crucial point in the future, specially in connection with the spectra of lanthanides and actinides [3]. These research topics reflected the importance and relevance of the Italian school (with Fermi and Majorana among others) before its tragic dissolution in 1938. Besides these articles, Racah published a few others of more mathematical nature (refs. 9-11, 21, 23, 24), like those referring to isotropic tensors in few dimensions. In the latter two articles he obtained an interesting method to evaluate multiplicities of induced representations (of the rotation group in three dimensions) without using the classical character theory, and providing recursive formulae in dependence of linear independent tensors subjected to special symmetry constraints. In some sense, these articles show Racah's interest in algebraic methods and can be seen as the germ of the tensor operator theory developed from 1942 onwards. In 1939, an important year for Racah for both personal as well as scientific reasons, new research topics and interests emerge with his emigration to Jerusalem. Once there, he started a systematical and rigorous work on spectroscopy, which would absorb most of his attention for the rest of his life, and establishing him as one of the most influential theoretical physicists.

The now famous series of four papers "Theory of Complex Spectra" (TCS) in the Physical Review (refs. 27, 30, 32, 35) is the basis for the modern approach to spectroscopic analysis, specially concerning the computations of energy levels. A new powerful technique to express interactions in terms of scalar products of tensor operators simplified considerably the computation of matrix elements, in opposition to previous approaches, the computations of which rapidly became too cumbersome and involved to be carried out for more complex spectra. In addition, adequate and subsequently fundamental notions like fractional percentage and recoupling coefficients (later

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representations of $SO(5)$.

[4] Jahn H A 1950 *Proc. Royal Society A, Math. Phys. Sciences* **201** 516; 1951 *Proc. Royal Society A, Math. Phys. Sciences* **205** 192.

named after him) were introduced, and their fundamental properties studied. The introduction of the new quantum number *seniority* v was the key to solve the designation problem of energy levels in configurations having several equivalent electrons. Although these notions were in principle applied to atomic spectra, they turned out to be also essential notions in nuclear physics (nuclear shell model), as was observed from the the mid fifties onwards. As a matter of fact, the quasi-spin introduced by Anderson, Wada, Takano and Fukuda in 1958, and adapted by Kerman to the study of pairing forces in nuclei was observed to be equivalent to a classification of states in terms of the seniority quantum number [4].[5] The fourth and last paper of the TCS series, appeared in 1949, not only extended to the f-shell the solution to the problem of designation of energy levels, but also constitutes a cornerstone for the use of group theoretical methods in physics. Specifically, the seniority scheme is defined in terms of irreducible representations of the orthogonal and symplectic groups[6]. The important role of the (quadratic) Casimir operators as natural candidates for labelling operators was shown in various reduction chains considered. Also for the first time an exceptional Lie group was used in the classification of f^n states. Even if the reduction involving G_2 was only a mathematical trick for the classification, it turned out to be the essential point that allowed to distinguish terms with the same quantum numbers L and S. The irreducible representations of the groups $SO(7)$ and G_2 were used to label the basis states within which the operators could be diagonalized. Selection rules arise then from the important Wigner-Eckart theorem. The reduction chain $SO(7) \supset G_2 \supset SO(3)$ is historically among the first examples of the so-called internal labelling problem, and in spite of later developments in the atomic shell theory, the sequences of groups used in the TCS series remained the central core around which most subsequent group chains have been constructed [6]

Although Racah's interest focused mainly in the interpretation of atomic spectra, he continued to work in the development of group theoretical methods. Following an invitation of R. Oppenheimer, he gave his famous lectures on Lie groups in Princeton in 1951 (ref. 67). The first three parts of these lectures contained the general theory on Lie groups, the classification of the (complex) semisimple algebras and the main facts concerning their representations. Even if the theory of classical Lie groups had been worked out earlier, most of the published texts were written in the opaque and difficult style of Cartan, Weyl and others, and were therefore of little attractive to the physicist. From the perspective of representation theory, various interesting results for physical applications were obtained. Among others, Racah showed that the total number of internal labels needed to distinguish states within an irreducible representation of a semisimple group G of rank l and dimension n was completely characterized by these quantities, *i.e.* $f = \frac{1}{2}(n - l)$. When using subgroups G' of G to label irreducible representations, these internal labelling split into three classes: those operators needed to characterize the representation and the components of its decomposition into G'-representations (Casimir operators of G and

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[5] In fact, at that time many nuclear physicists were reproducing some of Racah's results without being aware of their existence, as observed by Igal Talmi.

[6] This approach was later systematically expanded by Lipkin in [5]. It turned out that this ansatz was also adequate for the classification schemes in elementary particles.

G'), the missing label operators (subgroup scalars solving the degeneracies of the decomposition) and G'-internal operators to separate the states within each multiplet.[7]

The remaining lectures attempted to extend and generalize the methods used in the theory of complex spectra to the case of the nuclear shell model. Specifically, the classification and computation of nuclear states of mixed shells of nucleons with isospin and seniority in the LS-coupling was addressed. The final part presented a classification of nuclear interactions by means of tensorial methods, and applications to the computation of energy matrices. The typewritten version of these lectures became an essential reference with the years. Although these notes essentially contained the main facts to be used later in the classification schemes of elementary particles, the methods of these lectures remained largely unnoticed until the mid sixties, with the boom of group theory following the flavor classification of hadrons.[8] In this sense, in a short paper (refs. 41, 42) Racah showed the existence, for a semisimple Lie algebra of rank l, of exactly l independent operators in the generators that commute with the elements of the Lie algebras (i.e., the Casimir operators). This result, besides its importance in the labelling problem, expanded a well-known result of Casimir and Van der Waerden concerning the complete irreducibility of $SO\,(3)$-representations to all semisimple groups.[9] This work also presented an interesting approach to the invariant problem by means of differential operators, which would constitute in the future a powerful alternative to the formal computation in enveloping algebras. A beautiful application of these methods to nuclear physics can be found in Racah's contribution to the Farkas Memorial Volume (ref. 47), one of the fundamental references addressing to specific labelling problems in the analysis of nuclear structure.[10] In this paper, it was shown how the (quadratic) Casimir operator of a Lie group could be used to simplify the calculation of the levels of nuclear shells. Two cases were considered in detail: the LS-coupling with relevant reduction chain $SO\,(3) \subset SO\,(2l+1) \subset U\,(2l+1)$, and the jj-coupling, where the symplectic group $Sp\,(2l+1)$ emerged as the adequate tool to deal with the interactions. This fact was rapidly recognized and further developed by Flowers and Edmonds, among others.[11] It should be noted that, although Racah himself did not consider the symplectic groups in great detail, he implicitly used them by means of the seniority number scheme, as any v corresponds to an irreducible representation of $Sp(4l+2)$.[12] It was at this point that Racah realized that the notion of seniority v, introduced in atomic spectroscopy as a mere mathematical tool (like G_2 in the fourth part of

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[7] This fact was generalized to arbitrary groups by R. T. Sharp and his collaborators in the 70s by means of an analytical approach to the labelling problem. With this method, many of the classical result could be reformulated in a general frame, even connecting it with the (vector) coherent state formalism.

[8] See e.g. the contribution of Y. Ne'eman in [7].

[9] H. Casimir, B.L. van der Waerden, *Math. Ann.* **111**, 1 (1935).

[10] In spite of the historical importance of this paper, it seems to be quite unknown, or at least to have been overseen for a long time.

[11] The different character of LS and jj-coupling actually arose clearly when the seniority notion was introduced. Although the dimension of the groups coincide, their structure clearly reflected the symmetry or antisymmetry of wave functions. See e.g. I. Talmi 1962 *Reviews Mod. Physics* **34**, 704 or chapter 5 in Lipkin's book [5].

[12] See for example the book by B. R. Judd cited later in this work.

the TCS series), actually had an important meaning in nuclear spectroscopy. However, as late as 1958 this fundamental fact had not been widely accepted, as we can read in the introduction of Racah's contribution to the Rehovoth Conference in Nuclear Structure (ref. 55).[13] According to Racah's close collaborators, he did not feel very confident with some of the physical implications of nuclear spectroscopy,[14] which, in addition to the few experimental data available at that time, prevented him of applying his methods beyond some generic ansatz. It seems, however, that a great opportunity was lost, specially in connection with the emerging group theoretical methods in elementary particle physics in the beginning 60's. As example, Racah analyzed in one paper (ref. 53), almost at the same time but independently from Murai,[15] the notion of isotopic-reflections for the physical interpretation of the quantum number U (number of "iso-fermions") introduced earlier by Prentki and D'Espagnat.[16]

Another relevant notion introduced by Racah was the so-called "model-interactions" (nowadays "effective interactions"), basing on an idea published in 1934 by Bacher and Goudsmit[17], where they showed that the terms of an l^n configuration could be expressed as linear combinations of the terms of l^2 configurations in such a way that perturbations of l^n by all configurations differing from it by the states of two electrons and lying far from it were described by suitable modifications of the terms of l^2, being therefore independent on n. Racah developed these ideas in order to obtain complete sets of two-body effective interactions for the d^n configurations (refs. 44, 50, 62, 65, 70). Effective interactions were actively studied in the Hebrew University in order to improve the fit between theory and experiment in atomic spectroscopy [8].

With the emergence of the first big computers an efficient way to handle and contrast experimental data became available, and many procedures that prior to their invention had been avoided for reasons of computational difficulty (like effective diagonalization of matrices in very high orders) were possible. A big concern to Racah was the lack of experimental data to contrast his methods, and the possibility of using computers to compare the theoretical predictions with the experimental results did not escape to his attention. Following a visit to the National Bureau of Standards in 1954, Racah developed a great interest in the application of computers to theoretical spectroscopic analysis. During two years he developed additional programs (see ref. 57) to diagonalize matrices, comparing the resulting diagonalizations with experimental data and to compute line strengths. These computer procedures allowed to chose the problems and spectra according to their interest rather than to their practical possibility on mechanical calculators.[18] With the help of computers, many of the relevant complex (second) spectra with filling d shells

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[13] The footnote on page 159 of this note shows to what extent LS and jj-couplings were treated in the same way, without consideration to the important structural differences of the orthogonal and symplectic groups.

[14] See for example Prof. Unna's paper in this volume, where he recollects conversations with Racah at the Varenna school of 1960.

[15] Y. Murai 1956 *Nuclear Phys.* **1** 657. See also comments by A. Salam concerning these works.

[16] B. d'Espagnat, J Prentki 1956 *Nuclear Phys.* **1** 33

[17] Bacher RF and Goudsmit SA 1934 *Phys. Rev.* **46**, 948.

[18] These programmes were specifically designed for the WEIZAC, and very precise descriptions on the

(Iron, Palladium and Platinum groups) were analyzed in detail (see e.g. refs. 50, 58, 62, 63),[19] followed by the extremely complex spectra with filling f shells of rare earths (refs. 38, 49, 52, 61, 68, 69).[20] At the time of his death, the topic of the talk that Racah intended to give at the Zeeman Centennial Conference was to describe a new program to adjust calculated energy levels to observed ones, taking into account the g-factors of the levels. In the years after 1965, a combination of Racah's methods, powerful computer codes and more accurate instruments allowed to expand considerably the knowledge of the lanthanides, and opened new alternatives for finding the relative position of low-lying energy levels of opposite parities, as the infrared emission spectrum. The reference [3] discusses progress made from 1965 onwards, and describes the status and trends of lanthanide atomic spectra in 1978, when approximately 1000 complete or partial spectral analysis were available for 99 elements.[21]

In 1959 Racah and his cousin Ugo Fano wrote the monograph "Irreducible Tensorial Sets" (ref. 56),[22] which treated the algebra of tensor operators in great detail. In a first part, the theory was developed carefully from the first principles, paying special attention to subtle points like the consistent definition of phases of tensor operators. The second part dealt with quantum mechanical applications, although these were actually quite sporadic. Instead of analyzing concrete examples, the formalism was developed with great generality, leading to quite complicated formulae. These mere indications of applications was one of the major complaints about the book, accessible only for experts in the field. A quite puzzling fact about the book was the absence of group-theoretical argumentation.[23] Although this monograph was an important addition to the literature, it turned out to be mainly useful for experts already working with these techniques; for the beginners it constituted a quite hard reference. This however influential work was complemented with the books of A. R. Edmonds ("Angular Momentum in Quantum Mechanics", Princeton Univ. Press, Princeton, 1960) and B. R. Judd ("Operators Techniques in Atomic Spectroscopy", McGraw Hill Co., New York, 1963), written in a more direct style, making the algebraic formalism of Racah available to a more ample audience. Tabulations of angular momentum coupling coefficients [10, 11, 12], essential to the Racah algebra, further simplified computations and helped to derive new applications of the results. Special citation deserves B. G Wybourne book "Spectroscopic properties of Rare Earths", appeared in 1965, which stressed the importance of the Racah method for the analysis of lanthanides and actinides. Being himself

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machine's capability and the programs were given in ref. 57. In 1963 the computer was replaced by a PHILCO 2000, and shortly before Racah's death by the IBM 7040 model.

[19] The papers written in collaboration with Y. Shadmi and N. Spector (refs. 62 and 63 respectively) opened alternative ways to understand the intrinsic properties of interaction parameters.

[20] For an interesting account on the rare earths spectroscopy, see e.g. Wybourne B G 2004 *J. Alloys Compounds* **380**, 96.

[21] See also the discussion and tables in the first chapter of Cowan's book [9].

[22] An updated and enlarged version of this book was published 1996 by Fano in collaboration with A.R.P. Rau ("Symmetries in Quantum Physics ", Academic Press, N.Y.). In contrast to the original book, the expanded version was written with the intention of being useful as a textbook.

[23] See e.g. the review of this book by F. J. Dyson (*Physics Today* **13**, 38 (1960)).

an important contributor to the theory, Wybourne's treatment was everywhere closely related to the requirements of experimental spectroscopy. Most of the book is devoted to the spectra of free atoms and ions, with a final part dealing with rare-earth salts, showing how important these spectra were in the context of astrophysics and solid state physics. Approximately at the same time, an important and influential school was created in Vilnius, around specialists like Yutsis, Rudzikas and Vanagas, which would make serious efforts to motivate Racah's theory on physical grounds. An influential book[24] on the theory of angular momentum was written there [13], and consolidated the Vilnius school as one of the most relevant in the Soviet Union concerning Racah's methods. Starting from the classical reduction theory for the Kronecker products of irreducible representations by means of Clebsch-Gordan coefficients, arbitrary coupling schemes were considered, for which generalized Clebsch-Gordan, Wigner and Racah coefficients were defined. It seems that also in this book, the first graphical methods were developed, an approach that would evolve rapidly to simplify the formalism and provide new coupling schemes [14].[25]

Racah continued with calculations of atomic spectra until his death. With the members of his school and collaborators he systematically analyzed all known spectra in order to explain their structure. Specially for the rare earths, where the experimental data were rather scarce at the time, he tried to adapt and develop his methods to find some patterns in the high abundance of spectral lines and density of energy levels, in which no apparent regularity seemed to exist (ref. 61). Two factors were identified to be responsible for the complexity of these spectra, the competition between configurations and that of interactions. In the two posthumous references 68 and 69, the low levels of Erbium I and the 70 observed energy levels belonging to the subconfigurations $4f^6\left(^7F\right)4s4p$ of Samarium I were inspected in detail, correcting and enlarging recent work. Although Racah's collaborators continued with the this systematical analysis of spectra, his untimely death was a serious obstruction to the development of this programme.[26]

At the same time, he continued to develop general methods to nuclear spectroscopy. According to I. Talmi [15], shortly before his death he was working on a complete classification of the states in the seniority scheme of j^n configurations with nucleons. The group theoretical methods provided several degeneracies in the irreducible representations of $Sp\left(2j+1\right)$, with corresponding states having the same seniority quantum number, and a new quantum number to separate these degeneracies was required. How Racah's particular interests in this context would have evolved, finally focusing on problems he had not attacked directly, can only be a matter of speculation.

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[24] The impact of this work can actually be recognized from the fact that the first translation was published in Israel (Israel Program for Scientific Translations, Jerusalem, 1962).

[25] For historical developments of the graphical methods, see also El Baz E and Castel B 1972 *Graphical Methods of Spin Algebras in Atomic, Molecular and Particle Physics* (Marcel Dekker, NY); Varshalovich D A, Moskalev A N, Kersonskii' V K 1975 *Kvantovaya Teoriya Uglovogo Momenta* (Nauka, Leningrad).

[26] See e.g. Z. B. Goldschmidt's contribution in [7] and references therein. In this work an unpublished collaboration of Goldschmidt, Racah and Y. Bordarier is listed. Further work by collaborators of Racah can be found in the NIST Atomic Spectra Database at the address http://physics.nist.gov/PhysRefData/ASD/Html/ref.html

Summarizing, the legacy of G. Racah has been very important for atomic, molecular and nuclear spectroscopy, as well as for the definitive standardization of group theoretical methods in physics. His ideas and methods motivated other authors to further generalize and develop these techniques, and to apply them to physical and chemical problems far beyond their original conception. Here we have only made a very superficial description of Racah's work. A very detailed discussion of his papers and ideas can be found in Talmi's paper [16]. It has not been the author's objective to review Racah's influence in establishing theoretical physics in Israel, nor enumerating the high number of students and work that emerged from that school. The reader interested in these aspects, as well as personal accounts, can find excellent reviews written by direct collaborators of Racah in the articles of N. Zeldes [8] and I. Unna [17], as well as in the extensive bibliographies given there.

Publications of G. Racah

For completion in the exposition, we enumerate the scientific publications of G. Racah. The following list has been taken from [15], where the last references (appeared posthumously) have been completed and updated. Minor mistakes in the citation of references 62 and 68 have been corrected.

1. G. Racah and B. Rossi. *A proposito di un'osservazione di Stark sulla realta del moto assoluto*, Nuovo Cimento **6** 317 (1929)
2. G. Racah. *Sopra un esempio di trattazione quantistica di un fenomeno di interferenza*, Rendiconti della R. Academia Nazionale dei Lincei **11** 837 (1930) [Nuovo Cimento **7** 330 (1930)]
3. G. Racah. *Sopra l'elettrodinamica quantistica*, Rendiconti della R. Academia Nazionale dei Lincei **11** 1100 (1930) [Nuovo Cimento **7** 335 (1930)]
4. G. Racah. *Caratteristiche delle equazione di Dirac e principio de indeterminazione*, Rendiconti della R. Academia Nazionale dei Lincei **13** 424 (1931) [Nuovo Cimento **9** 28 (1932)]
5. G. Racah. *Sopra le strutture iperfini*, Nuovo Cimento **8** 178 (1931)
6. G. Racah. *Zur Theorie der Hyperfeinstruktur*, Zeitschrift für Physik **71** 431 (1931)
7. G. Racah. *Il Convegno di Fisica Nucleare*, Ricerca Scientifica **2** 416 (1931)
8. G. Racah. *Isotopic displacement and hyperfine structure*, Nature **129** 723 (1932)[27]
9. G. Racah. *Determinazione del numero dei tensori isotropi indipendenti di rango n*, Rendiconti della R. Academia Nazionale dei Lincei **17** 386 (1933)

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[27] This paper was later included in the book "Atomic Spectra" by W. R. Hindmarsh (Pergamon press, N.Y. 1967).

10. G. Racah. *Numero dei tensori isotropi e emisotropi in spazi a piu dimensioni*, Rendiconti della R. Academia Nazionale dei Lincei **18** 135 (1933)
11. G. Racah. *Numero dei tensori isotropi e emisotropi in spazi a piu dimensioni*, *Nota II*, Rendiconti della R. Academia Nazionale dei Lincei **20** 109 (1934)
12. G. Racah. *Sopra l’rradiazione nell’urto di particelle veloci, Nuovo Cimento* **11** 461 (1934)
13. G. Racah. *Sulla nascita degli elettroni positivi*, Nuovo Cimento **11** 477 (1934)
14. G. Racah. *Sul cosiddeto momento elettrico dell’elettrone,* Rendiconti della R. Academia Nazionale dei Lincei **20** 39 (1934)
15. G. Racah. *Sopra l’effeto Zeeman quadratico*, Nuovo Cimento **11** 723 (1934)
16. G. Racah. *Bemerkung zur Arbeit von Herrn Gamow: Empirische Stabilitätsgrenzen von Atomkernen*, Zeitschrift für Physik **93** 704 (1935)
17. G. Racah. *Vedute generali sulla constituzione dell nucleo atomico*, Bolletino di Matematica **31** 1 (1935)
18. G. Racah. *Production of electron pairs*, Nature **136** 393 (1935)
19. G. Racah. *Sulla nascita di coppie per urti di particelle elettrizzate*, Nuovo Cimento **13** 66 (1936)
20. G. Racah. *Sulla nascita di coppie per urti di particelle elettrizzate, Nota II*, Nuovo Cimento **14** 93 (1937)
21. G. Racah. *Sopra alcuni integrali collegati con gli integrali ellittici*, Rendiconti del R. Istituto Lombardo di Scienze y Lettere **70** 340 (1937)
22. G. Racah. *Sulla forma lagrangiana delle forze elettromagnetiche*, Rendiconti della R. Academia Nazionale dei Lincei **25** 233 (1937)
23. G. Racah. *Sopra i tensori isotropi che presentano particolari simmetrie, Nota I,* Rendiconti della R. Academia Nazionale dei Lincei **25** 475 (1937)
24. G. Racah. *Sopra i tensori isotropi che presentano particolari simmetrie, Nota II,* Rendiconti della R. Academia Nazionale dei Lincei **25** 615 (1937)
25. G. Racah. *Sulla simmetria tra particelle e antiparticelle*, Nuovo Cimento **14** 322 (1937)
26. G. Racah. *Ricerche moderne sulle teorie nucleari*, Societa Italiana per il progresso delle scienze **16** 82 (1938)
27. G. Racah. *Theory of complex spectra I*, Physical Reviews **61** 186 (1942)
28. G. Racah. *On a new type of vector coupling in complex spectra*, Physical Review **61** 537 (1942)

29. G. Racah. *On the deep configuration of Cobalt*, Physical Review **61** 537 (1942)
30. G. Racah. *Theory of complex spectra II*, Physical Review **62** 438 (1943)
31. G. Racah. *On the configuration* ll''s, Physical Review **62** 523 (1943)
32. G. Racah. *Theory of complex spectra III*, Physical Review **63** 367 (1943)
33. G. Racah. *On the structure of* $\mathrm{Mo(CN)}_8^{-4}$, J. Chemical Physics **11** 214 (1943)
34. G. Racah. *On the self-energy of the electron*, Physical Review **70** 406 (1946)
35. G. Racah. *Theory of complex spectra IV*, Physical Review **76** 1352 (1949)
36. G. Racah. *On the decomposition of tensors by contraction*, Reviews Modern Physics **21** 494 (1949)
37. G. Racah. *On the calculation of nuclear levels*, Helvetica Physica Acta **23** 229 (1950)
38. G. Racah. *On the spectrum of* Th III, Physica **16** 651 (1950)
39. G. Racah. *Nuclear coupling and shell model*, Physical Review **78** 622 (1950)
40. G. Racah and N. Zeldes. *On the spins of* Li^6 and B^{10}, Physical Review **79** 1012 (1950)
41. G. Racah. *Sulla caratterizzazione delle rappresentazione irriducibili dei gruppi semisimplici di Lie*, Rendiconti della R. Academia Nazionale dei Lincei **8** 108 (1950)
42. G. Racah. *On the characterization of the rows and columns of the representations of the semisimple Lie groups,* Proceedings of the International Congress of Mathematicians 1950, Vol 1, p. 467
43. G. Racah. *Directional correlations of successive nuclear radiations,* Physical Review **84** 910 (1951)
44. G. Racah. $L\,(L+1)$ *correction in the spectra of the Iron group*, Physical Review **85** 381 (1952)
45. G. Racah. *Term values of the* f^3 electron configuration, Current Science 21 67 (1952)
46. G. Racah and I. Talmi. *The pairing property of nuclear interactions,* Physica **18** 1097 (1952)
47. G. Racah. *Nuclear levels and Casimir operators,* Farkas Memorial Volume, Research Council of Israel, Jerusalem 1952, p.294
48. G. Racah. *The competition between the low configurations in the spectra of the Iron group,* Bulletin of the Research Council of Israel III 290 (1954)
49. G. Racah. *Some new levels in the spectrum of* Yb II, Bulletin of the Research Council of Israel III 437 (1954)

50. G. Racah. *The present state and problems of the theory of atomic spectra,* Proceedings of the Rydberg Centennial Conference on Atomic Spectroscopy, Lund 1955, p.31

51. G. Racah. *A search for new quantum numbers in nuclear configurations*, Proceedings of the 1954 Glasgow Conference on Nuclear and Meson Physics, Pergamon Press, London and New York 1955, p.126

52. G. Racah. *Intercombination in the spectrum of* CeII, Bulletin of the Research Council of Israel **5A** 78 (1955/56)

53. G. Racah. *Remarques sur une formulation mathématique du modèle de Gell-Mann,* Nuclear Physics **1** 302 (1956)

54. G. Racah. *Coupling schemes in atomic spectra,* Bulletin of the Research Council of Israel **7F** 188 (1957/58)

55. G. Racah. *The seniority quantum number and its applications to nuclear spectroscopy,* Proceedings of the Rehovoth Conference on Nuclear Structure, North Holland Publishing Co, Amsterdam 1958, p.155

56. G. Racah and U. Fano. *Irreducible tensorial sets,* Academic Press, New York 1959

57. G. Racah. *The use of the Weizac in theoretical spectroscopy,* Bulletin of the Research Council of Israel **8F** 1 (1959)

58. G. Racah and Y. Shadmi. *The configurations* $(3d+4s)^n$ *in the second spectra of the Iron group*, Bulletin of the Research Council of Israel **8F** 15 (1959)

59. G. Racah. *Theory of Lie Groups*, Nuovo Cimento Supplemento **14** 67 (1959)

60. G. Racah. *Four dimensional orthogonal groups,* Nuovo Cimento Supplemento **14** 75 (1959)

61. G. Racah. *Vector coupling and notations in the rare-earths spectra*, Journal of the Optical Society of America **50** 408 (1960)

62. G. Racah and Y. Shadmi. *Q correction in the spectra of the Iron group*, Physical Review **119** 156 (1960)

63. G. Racah and N. Spector. *The configurations* 3d^{n}4p *in the second spectra of the Iron group*, Bulletin of the Research Council of Israel **9F** 75 (1960)

64. G. Racah. *Mathematical techniques*, Proceedings of the International School of Physics "Enrico Fermi", XV Course: Nuclear Spectroscopy, Academic Press, New York and London 1962, p.1

65. G. Racah. *Model interactions in atomic spectroscopy*, Journal of the Quantitative Spectroscopy and Radiative Tranfer **4** 617 (1964)

66. G. Racah. *Lecture on Lie Groups*, Group Theoretical Concepts and Methods in Elementary Particle Physics, F. Gürsey (ed.), Gordon and Breach, New York 1964, p.1

67. G. Racah. *Group Theory and Spectroscopy*,[28] Ergebnisse der exakten Naturwissenschaften (Springer Verlag Berlin) **37** 27 (1965)

68. G. Racah, Z. B. Goldschmidt and S. Toaff. *Low odd levels of Erbium*, Journal of the Optical Society of America **56** 407 (1966)

69. G. Racah and U. Ganiel. *Subconfigurations* $\mathrm{f}^6(^7\mathrm{F})\mathrm{sp}$ in Sm I, Journal of the Optical Society of America **56** 893 (1966)

70. G. Racah and J. Stein. *Effective interactions in* l^n *configurations*, Physical Review **156** 58 (1967)

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References

[1] O. Hahn, F. Straßmann, *Naturwiss.* **27**, 89, 163 (1939).

[2] S. Flügge, *Naturwiss.* **27**, 544 (1939).

[3] J. F. Wyart, *J. Opt. Soc. Am.* **68**, 197 (1978).

[4] P. W. Anderson, *Phys. Rev.* **112**, 1900 (1958); Y. Wada, F. Takano, N. Fukuda, *Prog. Theor. Phys. Japan* **19**, 597 (1958); A. K. Kerman, *Ann. Phys.* **12**, 300 (1961).

[5] H. Lipkin. "Lie Groups for Pedestrians" (North-Holland Publishing Company, Amsterdam 1962).

[6] B. R. Judd, *Rep. Prog. Phys.* **48**, 907 (1985).

[7] F. Bloch, S. G. Cohen, A. de-Shalit, S. Sambursky and I. Talmi. "Spectroscopic and Group Theoretical Methods in Physics" (North-Holland Publishing Company, Amsterdam 1968).

[8] N. Zeldes, *Arch. Hist. Exact Sci.* **63**, 289 (2009).

[9] R.D. Cowan. "The Theory of Atomic Structure and Spectra" (Univ. of California Press, Berkeley CA 1981).

[10] M. Rotenberg, R. Bivins, N. Metropolis, J. K. Wooten. "The 3-J and 6-J Symbols" (Technology Press, MIT, Cambridge, MA 1959)

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[28] First mimeographed in Princeton in 1951, later reproduced in CERN prior to its publication in the Springer Tracts in Modern Physics.

[11] C. W. Nielson, G. F. Koster. "Spectroscopic Coefficients for the p^n, d^n and f^n Configurations" (MIT. Press, Cambridge, MA 1963)

[12] Ya. I. Vizbarayte, I. I. Glenbotzkii', R. I. Kuraziya, T. D. Strotzkite, V. I. Uldynitze. "Tablitzii' 9-j koeffizientov dlya tzelykh znachenii' parametrov s odnim parametrom ravnym edinitze" (Akad. Nauk SSSR, Moskva 1959).

[13] A. Yutsis, J. Levinsonas, V. Vanagas. "Matematicheskii' Apparat Teorii' Momenta Kolichestva Dvizheniya (Akad. Nauk Litovsk. SSR, Vilna 1960); R. I. Karaziya, Ya.I. Vizbaraite, A. B. Rudzikas, A. P. Yutsis, "Tablitsy dlya rascheta matrichnykh elementov atomnykh velichin" (Acad. Nauk, Lit. SSR, Moskva 1967).

[14] E. Balcar, S. W. "Introduction to the Graphical Theory of Angular Momentum" (Springer, NY 2009)

[15] I. Talmi, *Nuclear Physics* **83**, 1 (1966).

[16] I. Talmi, *Adv. Nucl. Phys.* **27**, 1 (2003).

[17] I. Unna, *Phys. Perspect.* **2**, 336 (2000).

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Racah algebra and x-ray *sum rules* in magnetism of solids

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Abstract

This is an overview of the role played by G. Racah's "Theory of Complex Spectra" in new experiments based on x-ray spectroscopy, and mainly on magnetism of solids. The "Theory of Simple Spectra" by B. T. Thole, G. van der Laan and P. Carra is presented and some of the fields of interest reviewed.

1 Introduction

1.1 The Theory of Complex Spectra

In a remarkable series of Physical Review papers [2, 3, 4, 5] Giulio Racah established in less than a decade the group-theoretical basis allowing the correct interpretation of spectroscopy experiments on non-trivial atomic, nuclear and elementary particle physics.

Previously to Racah's pioneering work, only simple and rather particular cases, involving a small number of angular momenta could be correctly tackled, involving lengthy calculations of Slater integrals even in the most favourable cases. The standard book was E. U. Condon and G.H. Shortley's "The Theory of Atomic Spectra" [1]. In practice, the calculations were usually unaffordable. G. Racah developed a spherical tensor technique, the so called *Wigner-Racah algebra*, allowing to calculate the energies of electronic configurations in a growing scale of difficulty: first two electrons and rather simple three-electron configurations [2], then the more complex situations for $l = 1$ and 2 (describing the electronic shells of transition metals of the d series) [3, 4], and finally, the f^n configurations [5] which from an electronic-shell point of view correspond to lanthanides and actinides. Thus, the four-paper series provides the full artillery needed to interpret atomic spectroscopy experiments along the whole periodic table of the elements, and to understand in detail the origin of the main ingredient of solid-state magnetism: electronic angular momenta.

1.2 Crystal field and magnetism

Magnetism of solids is no more (but no less) than addition of electronic angular momenta and the (usually complex) interactions between them. The role of Racah algebra in our understanding of magnetism is therefore a very important one, and its impact spans on several areas. It has been traditionally linked to the theory of crystal field interaction. The combination of Hans Bethe's crystal field theory [6] and Giulio Racah's algebra allowed Y. Tanabe and S. Sugano [7, 8, 9] to properly describe the energies and electronic states of d transition ions within solids (strong and intermediate crystal fields). The solution depends on the symmetry of the site occupied by the ion. It is easy to show that in most cases, the mixing of the free-ion electronic states by the crystal field interaction has a very small (or zero) expectation value for the orbital magnetic moment in a given axis of quantisation. This is the so-called "quenching" of the orbital momentum by crystal electric field, which leads to the spin-only magnetic moments of $3d$ magnets, in very good agreement with experiment [10]. Only the spin-orbit interaction, weaker than the crystal field in d ions injects some unbalance in the otherwise symmetric $\langle L_z \rangle = 0$ situation. This fact is of the highest interest in magnetism and its applications, as the orbital magnetic moment is the microscopic origin of the magnetic anisotropy energy and therefore, of any useful magnet. However, the separate determination of orbital magnetic moments has been an elusive objective of the classical magnetometries.

The crystal field theory had an remarkable success explaining the puzzling spectra obtained from *rare-earth* ($4f$) ions. The solution was supplied in a simultaneous and independent manner by B. R. Judd [11] and G. S. Ofelt [12]. Lanthanides are very different to $3d$ ions: the $4f$ unfilled shell is strongly screened by the occupied $5s^2 5p^6 6s^2$ shells, and the crystal field interaction has to be treated as a perturbation of the spin-orbit interaction. The Hund rules determine the L, S, and J values of the ground state term, which is splitted in mixed $|J_z\rangle$ states by crystal fields. The details of the spectra are very complicated, and the magnetic properties of the ground state usually hard to predict, although the bases of the theory are fully developed [13]. The usually large orbital momenta in rare earths are at the origin of its huge magnetic anisotropy. Indeed, the *metallurgical recipe* [14] of high-quality modern magnets stands on the (ferromagnetic) addition of the cheap magnetic moment of Fe or Co, to the extremely anisotropic moment of Nd or Sm. The development of low-prize, small-volume, high-power rare-earth – iron magnets has contributed significatively to change our everyday technology in the last two decades.

1.3 Some technical achievements

The application of Racah algebra methods to interpret interesting spectra in chemistry and solid state physics required the evaluation of matrix elements of Coulomb or multipole interaction operators between atomic or molecular states in non-trivial cases. Three main steps were needed to fulfill this objective: the developement of graphical methods (the Yutsis graphs) for representing the recoupling coefficients and reduction rules leading to summation formulae [15], Judd's reformulation of Racah's work on a second quantization basis [16] and the implementation of computer codes allowing to timely calculate spectra in different energy ranges and experiments. In particular, the Hartree-Fock based atomic structure code by Robert D. Cowan has had a great impact on solid-state and molecular spectroscopy [17, 18]. The extension of the Hartree-Fock calculations with hybridization and point group symmetry, as is mandatory in molecules and solids, allowed to calculate the transitions from the ground state to every allowed final state.

The success of the implementation of the *Theory of Complex Spectra* to solids and molecules (now usually referred to as "*multiplet theory*") is remarkable: in principle it is possible to analyze not only x-ray absorption spectra, but also photoemission, resonant x-ray scattering, as well as polarisation dependent experiments. Such a calculation should allow to understand the local electronic structure (and therefore the chemical bonding) of molecules and solids. However, usually there are too many relevant unknowns which complicate the fulfillment of such an ambitious program: the relative strength of spin-orbit interaction and exchange, the details of crystal field (in particular the role played by conduction electrons), among others which seriously difficult our ability to determine the final states, specially in solids. Properly performing "multiplet calculations" is complicated, and in practice almost exclusively specialized theorists are succesfully devoted to them (even if a "*Hitchhiker's guide*" to the subject is available [19]).

2 Theory of Simple Spectra

With the advent of condensed-matter dedicated synchrotrons *circa* 1980, x-ray absorption and emission become routine techniques. In those years, the volume of scientific production in molecular chemistry, condensed matter physics and materials science was too large to undertake the effort of studying the details of each spectra. Only some special cases deserved to be studied with such degree of refinement. Moreover, after 1990, several facts opened the possibility to study not only the spectra but its variations with other parameters. In particular, the possibility to choose the polarisation of synchrotron radiation (circular or linear in any direction) thanks to new sources known as "insertion devices" and a greatly improved quality of the experimental spectra (due to advances in brilliance, stability of the beam and detector sensitivities), allowed to study the dependence of absorption with the polarisation of the incoming beam. These *dichroic* spectra, among which the X-ray Magnetic Circular Dichroism (XMCD) has become the paradigmatic example [20, 21, 22], are harder to fit with the whole Racah-algebra machinery than absorption itself: small variations in the spin-orbit or exchange energies of initial or final states provoke dramatic differences in dichroic spectra, as XMCD intensities are very often not larger than 1%.

After the advent of third-generation synchrotron radiation sources in the 1990's, XMCD become an almost-routine technique, although pioneer works were performed earlier in Munich [23] and Groningen [24]. In 1984, Theo Thole joined George Sawatzky's group at the University of Groningen as a postdoc. This group was measuring X-ray spectroscopy of transition metals in solids and molecules at the *Anneau de collision* (ACO) in Orsay, and Thole's subject was to write a code allowing to simulate the experimental spectra. Although the initial suggestion was to start from scratch, finally it was decided to adapt Cowan's codes by extending the Hartree-Fock calculations with hybridization and point group symmetry, as is mandatory in molecules and solids. Theo's code for hybridization was written in collaboration with Akio Kotani, one of the founding fathers of the present japanese spectroscopy school. By the way, the original routine which applied Wigner-Eckart theorem to obtain reduced matrix elements in any point group, which had been developed by P.H. Butler [25], was called "RACAH" by Thole. While Thole was working on the theoretical spectroscopy program, he coincided in Groningen with G. van der Laan, a former fellow student. Together, they envisaged a research program aiming to provide experimenters with simpler analysis tools. Thole and van der Laan coined this program "*Theory of Simple Spectra*" [26] in clear reference to Racah's original Physical Review papers. These tools took the form of *sum rules*, relating the integrals of the spectra to the expected values of different quantum operators in the ground state.

2.1 The spin-orbit sum rule

Theo Thole and Gerrit van der Laan [27, 28] first developed a sum rule relating the integral of the unpolarized x-ray absorption spectrum over the spin-orbit split $j = l \pm 1/2$ core edges to the expectation value of the ground-state spin-orbit operator. A systematic study of the *branching ratio* in X-ray absorption (the ratio between the absorption observed at the L_3 ($2p_{3/2}$) and L_2 edges ($2p_{1/2}$) evidenced strong deviations from the statistical value for the spin-orbit split p to d absorption in transition metals and d to f absorption in rare-earth metals, which were not understood at that time. By means of graphical methods which were carefully checked by numerical computation, Thole showed that the branching ratio was directly proportional to the spin-orbit coupling in the ground state: only if L and S are good quantum numbers, the branching ratio is purely statistical (2:1 in $L_{3,2}$ edges). Any deviation from the statistical value indicates spin-orbit splitting in the initial (i.e. ground) state.

The expectation value of the spin-orbit operator $\mathcal{Z} = \sum_i \mathbf{l}_i \mathbf{s}_i$ can be determined by a simple measurement of the branching ratio, thanks to the linear relationship (which is exact for dipole transitions $l^n \to cl^{n+1}$) [28]:

$$B_j(\Psi) = \frac{2j+1}{2(2c+1)} \pm A(c,l,n)\langle\Psi|\mathcal{Z}|\Psi\rangle \tag{1}$$

where the ± sign is for the two $j = c \pm 1/2$ edges, respectively. The proportionality constant $A(c, l, n)$ depends on the total angular momentum of the core hole c, the l of the valence electron and on the number of electrons n, and was tabulated on the original manuscript [28]. In Fig. 1 the $L_{2,3}$ x-ray absorption of a sample of Pt_{13} clusters dispersed in the cages of a Na-Y zeolite structure [29] is shown. Besides its potential interest in fuel catalysis, this experiment exemplifies how easy is to put in evidence a non zero $\langle\mathcal{Z}\rangle$ value. However, although related with the magnetic moment of a system, the sum rule on the expected value of the spin-orbit operator has for some time lay dormant. However, it has recently made a comeback in the research on actinides, where the spin-orbit interaction is very strong [30]. Nevertheless, the use of this first sum-rule has been relatively scarce: the impact of Refs. [27] and [28] has been stabilized with less than a *hundred* citations, while the magnetic sum rules to be presented later have received more than one *thousand* each since 1992, and counting.

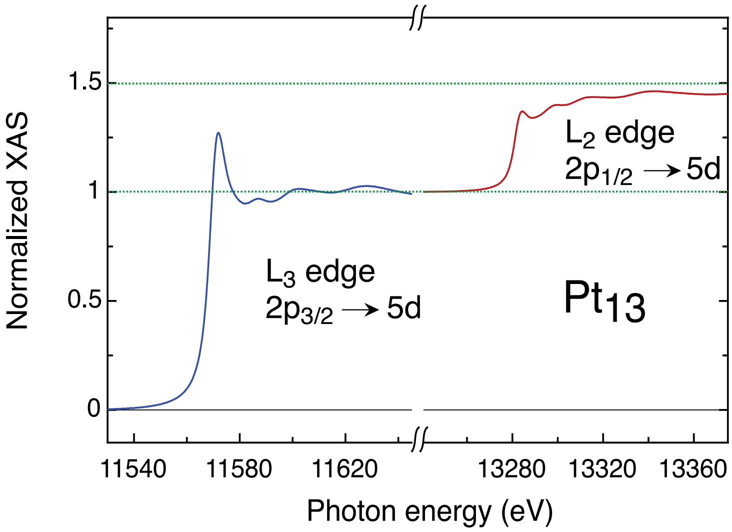

Figura 1.— X-ray absorption at the Pt $L_{2,3}$ edges recorded on a sample of Pt_{13} clusters. The departure of the statistical 2:1 branching ratio is exemplified after normalizing the signals to 1 at the L_3 edge: the XAS signal well above the edge is clearly below 1.5, indicating a non zero $\langle \mathcal{Z} \rangle$ value.

2.2 The XMCD sum rules

XMCD is the difference of absorption $\Delta\mu = \mu^{-1} - \mu^{+1}$ of left (-1) and right (+1) circularly polarized light due to the dependence of the selection rules with the relative orientation of the photon helicity and the angular momentum of the absorbing atom. Experimentally, this relative orientation can be chosen by an applied magnetic field or by changing the polarisation.

It is relatively easy to show [31] that, in selected cases, the XMCD signal is proportional to the magnetization of the absorbing sublattice. As the edge energies are characteristics of each element, XMCD is an element-specific, extremely powerful magnetometry. XMCD is obviously related with the *optical activity* induced in matter by a longitudinal magnetic field as first shown by Faraday in the visible range.

2.2.1 THE ORBITAL SUM RULE

Systematic trends of the integrated dichroic signal, and a dependence of integrated intensity on the spin-orbit splitting became evident. Again by using diagrammatic techniques Thole was able to derive [32] the following relationship between the expected value of the third component of the orbital moment in the ground state;

$$\langle L_z \rangle = \frac{2l(l+1)(4l+2-n)}{l(l+1)+2-c(c+1)} \times \frac{\int_{j_+ + j_-} d\omega(\mu^{-1} - \mu^{1})}{\int_{j_+ + j_-} d\omega(\mu^{-1} + \mu^{1} + \mu^{0})} \tag{2}$$

in units of $\hbar$, where the total angular momentum of the core hole and the valence electron are respectively c and l and n is the number of electrons in the valence shell (therefore, $(4l+2-n)$ is the number of holes available in the absorbing shell in the ground state). The integral $\int_{j_+ + j_-} d\omega(\mu^{-1} + \mu^{1} + \mu^{0})$ is 3 times the averaged absorption for unpolarized light, and is introduced into the equations for normalization. Note that (2) is independent of the radial integrals.

2.2.2 The spin sum rule

M. Altarelli found a simpler proof of the orbital sum rule (2), based on one-electron Slater determinants [33]. This finding paved the way to the derivation, by Carra and Thole, of the second sum rule for magnetic dichroism [34], which related the spin moment and the magnetic dipole term to the weighted difference of the spin-orbit split dichroic signal:

$$\frac{\int_{j_+} d\omega(\mu^{-1} - \mu^{1}) - [(c+1)/c] \int_{j_-} d\omega(\mu^{-1} - \mu^{1})}{\int_{j_+ + j_-} d\omega(\mu^{-1} + \mu^{1} + \mu^{0})} \times (4l+2-n) =$$
$$\frac{c(c+1)+2-l(l+1)}{3c} \langle S_z \rangle - \frac{l(l+1)\,[l(l+1)+2c(c+1)+4] - 3(c-1)^2(c+2^2)}{6lc(l+1)} \langle T_z \rangle \tag{3}$$

where $\langle T_z \rangle$ is the magnetic dipole operator, whose expectation value provides a measure of the anisotropy of the field of the spins when the atomic cloud is distorted, either by the spin-orbit interaction or by crystal-field effects [35]. The expected value of the spin moment can be accurately obtained for those cases in which $\langle T_z \rangle$ can be determined: $\langle T_z \rangle$ is small in cubic 3d systems, it can be analytically calculated in $\mathrm{M}_{4,5}$ edges of rare earths and actinides, and it is zero in $l = 0$ configurations. In other cases, $\langle T_z \rangle$ can be extracted from angular-dependent measurements. Otherwise, only the value for an "effective spin" operator, mixing $\langle S_z \rangle$ and $\langle T_z \rangle$ can be experimentally determined.

The theory department of the European Synchrotron Radiation Facility (ESRF), directed first by Massimo Altarelli and later by Paolo Carra, grouped the efforts of a small but very active team of scientists that Theo Thole joined for long stays during the first years of the nineties. Their work, in close contact to the development of several x-ray techniques at the ESRF beamlines [36, 37, 38, 39, 40] has had a worldwide impact in the development of x-ray scattering techniques and the design of new sources.

Unfortunately, Theo Thole (1950-1996) and Paolo Carra (1952-2005) passed away by far too soon. Of the pioneering group, only Gerrit van der Laan worked further on the development of the *Theory of Simple Spectra*, looking forward and beyond XMCD sum rules to higher statistical momenta, to extract the maximum information from experimental x-ray spectra [41].

3 The short and winding way to the bottom

In his famous talk *"There's plenty of room at the bottom"* [42], Richard Feynman foresaw the advent of a nanotechnological future, which today is a reality in condensed matter research and also partly in consumer electronics. Third generation synchrotron sources are very well suited to study nanoscopic systems due to its extreme brilliance: the x-ray spots are microscopic while maintaining an extremely high photon flux. This allows the study of extremely small samples. For example, the amount of Pt probed in the experiment of Fig. 1 is tiny, and the possibility to study in detail its magnetism, as shown in Fig. 2 and Ref. [29] is somehow astonishing. Indeed, one of the most reassuring properties of XMCD is its element selectivity, which ensures that the observed magnetization in Fig. 2 has its origin in nothing but Pt, ruling out any spurious source of magnetism, in contrast with other highly sensitive magnetometries [43, 44, 45].

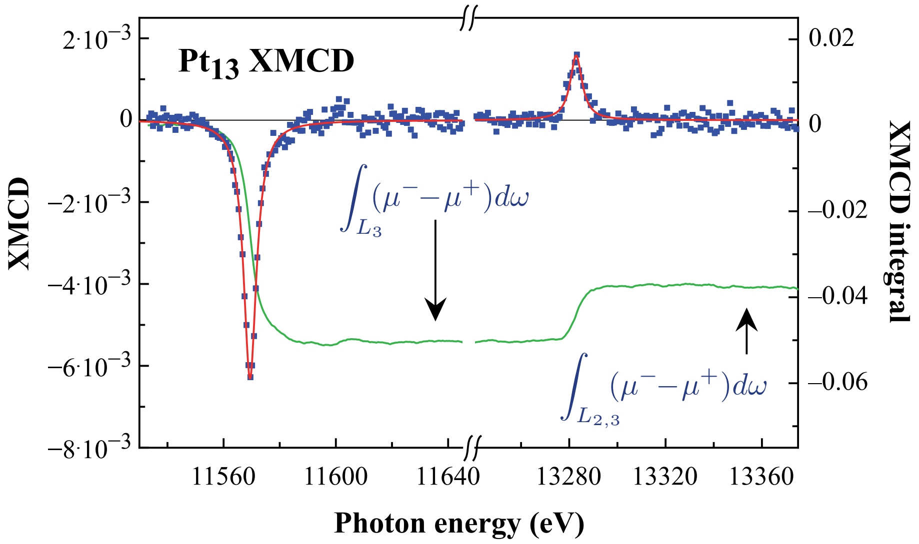

Figura 2.— X-ray Magnetic Circular Dichroism at the Pt $L_{2,3}$ edges recorded on a Pt_{13} cluster, in the same units of Fig. 1. The observed XMCD signal is clearly larger than expected for usual Pauli paramagnetism in bulk Pt. This demonstrates the establishment of a magnetic moment on Pt_{13} clusters due to a finite-size effect on the Pt electronic structure.

As clearly shown in Fig. 3 the integrals involved in the magnetooptical sum rules (equations 2 and 3) are relatively simple to obtain, except in the case of extremely small magnetic moments ($\mu \leq 10^{-3}\mu_B$).

4 Orbital moments and magnetic anisotropy

Among many examples in the recent literature, sum rules have been recently applied to study the magnetic moments of molecules as Fe-phtalocyanine (FePc). Appart of its large industrial uses, metal phthalocyanines are simple model molecules for the understanding of the electronic properties of metals in complexes. In spite of extensive work on them, their magnetic properties are not fully understood. In FePc, the Fe atom has square-planar coordination with four pyrrolic N atoms (see Fig. 3, left). In the bulk and thin films these planar molecules form linear chains by columnar stacking. The molecule fourfold axis is tilted with respect to the crystal b axis by an angle ϕ. In the bulk form two phases appear; the α-FePc with a tilting angle of $\phi = 26.5°$, and the β-phase with $\phi = 44.8°$. The former becomes ferromagnetic below $T_C \sim 10$ K in the bulk form while the latter is paramagnetic down to liquid helium temperatures.

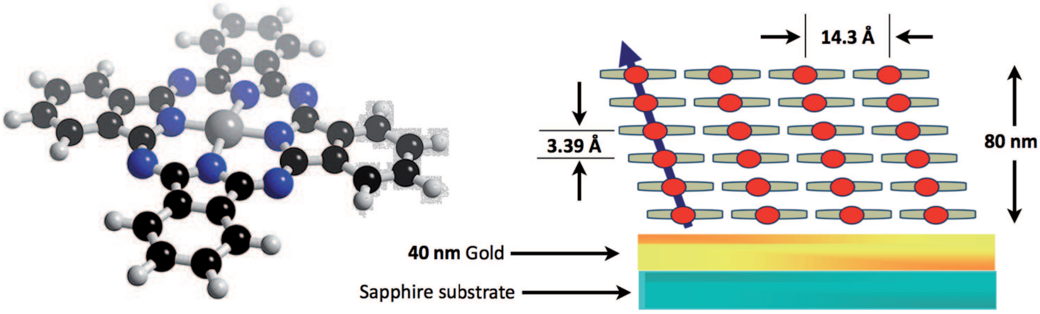

Figura 3.— Left: Artist view of an FePc molecule. The Fe is the central atom (gray) bonded to the 4 pyrrolic N (blue). Other four N atoms (blue) bridge the organic structures formed by the C (black) and H (white) atoms. The molecule is plane to a very good approximation. Right: Schematic view of the columnar film FePc sample indicating its dimensions.

Thin films of FePc are deposited on a smooth gold substrate with the molecule plane lying flat on the substrate plane. The thin film sample in this work was prepared in an organic molecular beam epitaxy (OMBE) system at the Physics Department of the UCSD. In thin films grown by OMBE the molecule plane orientation is set by a proper substrate selection and the growth conditions. In order to obtain α-phase FePc films with the molecule plane parallel to the sapphire substrate, first a 40 nm nominal thickness Au buffer layer was deposited. Without breaking vacuum, the FePc was deposited from a crucible set to 350 °C, while the substrate was maintained at 150 °C to increase the crystallite size. The typical growth rate was 0.9 Å/s. The FePc deposition rate is determined by means of a quartz crystal monitor before and after the deposition. The FePc thickness of the investigated sample was 80 nm.

We have measured a sample of such columnar thin films as shown in Fig. 4 (right). The orientation of a column parallel to the substrate can not be controlled, and therefore any anisotropy within the plane is averaged out in the experiment. The relevant x-ray spectra obtained in normal incidence are shown in Fig. 4. Panel *a* shows the x-ray absorption spectra in the vicinities of the Fe $L_{2,3}$ edges recorded with left- (blue) and right-polarised light (red), together with the integral of the averaged, unpolarised absorption, the normalization value appearing in eqns. 2 and 3. The XMCD signal (green) is shown in the panel *b* of Fig. 4. In Fig. 4(c) the values of the

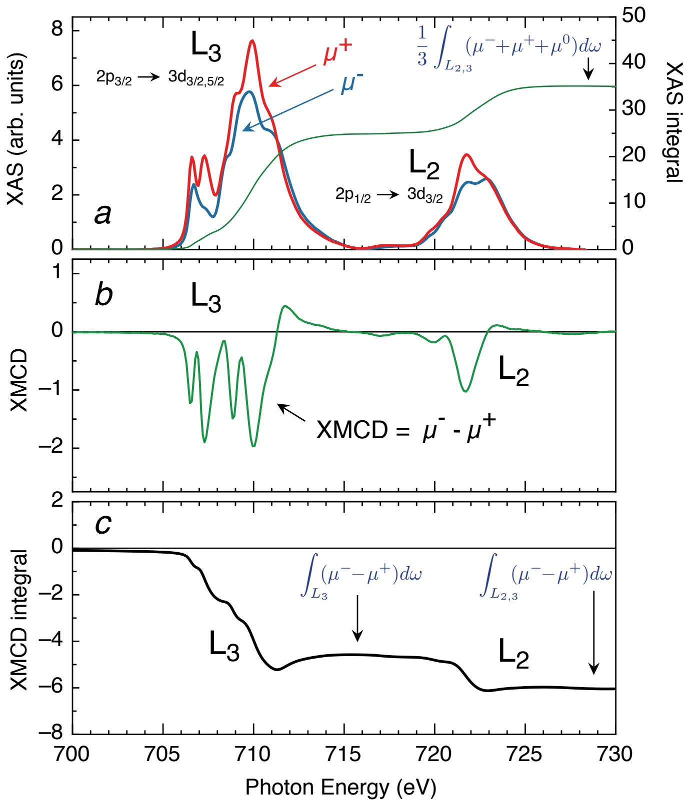

Figura 4.— *a)* X-ray absorption spectra with right (red) and left (blue) circularly polarised light at the Fe $L_{2,3}$ edges on the FePc thin film sample. The integral of the averaged unpolarised absorption is also shown (green). *b)* X-ray Magnetic Circular Dichroism obtained from the XAS spectra shown in the upper pannel. *c)* Integral of the XMCD signal. Panels *a)* and *c)* identify the relevant integrals in the sum rules (2) and (3) with the experimental values.

integrated XMCD with upper integration limits at the respective arrows, have been depicted. Similar spectra and analysis are performed at different incidence angles, from normal to grazing incidence. The detailed analysis has been published [46] and the results are shown in Table 1.

The orbital moment is anisotropic, being largest when the applied field is parallel to the xy molecule plane, which is in agreement with magnetization results [46]. Its value is $m_L^{xy} = 0.53 \pm 0.04\mu_\mathrm{B}$. In spite of the applied approximations, and the inherent experimental uncertainty, the existence of an extraordinarily large, highly unquenched orbital moment in FePc is proven beyond doubt.

With the experimentally determined values of m_L^{xy}, m_L^z, and m_T^z it is possible to derive an estimation of the Magnetocrystalline Anisotropy Energy originating from spin-orbit coupling by means of the Bruno-van der Laan model [47, 48]:

$$\Delta E_{SO} = -\frac{G}{H}\left(\frac{\xi_{3d}(m_L^z - m_L^{xy})}{4\mu_\mathrm{B}} + \frac{\xi_{3d}^2((\frac{21}{2})(\frac{3}{2})m_T^z + A)}{\Delta E_{ex}\mu_\mathrm{B}}\right) \tag{4}$$

where G/H ≈ 0.2 for transition metals, $\xi = 0.05$ eV for Fe, and $\Delta E_{ex} = 1$ eV is the energy

Table 1.— The magnetic moment (orbital, spin and dipolar, in units of μ_B) obtained from the XMCD sum rule results, and the calculated orbital to spin moment ratio.

m_L^{xy}	m_L^z	m_S	m_T^z	m_T^{xy}	m_L^{xy}/m_S
0.53(4)	0.29(5)	0.64(5)	0.074(5)	-0.037(5)	0.83(4)

shift between the majority and minority states. The first term corresponds to the anisotropy originating from the difference in orbital moment between the perpendicular and parallel directions to the substrate plate (thus of orbital origin), and the second term from the intra-atomic dipolar term, describing the anisotropy in the spin density. Replacing the numerical values, one gets $\Delta E_{SO} \approx +6.0\times 10^{-4} - 5.3\times 10^{-4} = 7\times 10^{-5}$ eV. Thus, the orbital term and the dipolar term are of the same order of magnitude and are competing with each other. The sign is positive, thus favoring xy anisotropy. Since the anisotropy field was estimated as $\mu_0 H_A = 0.6$ T, the anisotropy (volume) constant can be evaluated as $|K_1| = \mu_0 H_A M_s/2$, yielding $K_1 = -2.2 \times 10^3$ J/m^3, or $\Delta E_{SO} = 2.1 \times 10^{-5}$ eV/atom, assuming the specific volume of Fe atoms as $v = 1.48 \times 10^{-28}$ m^3, as in α-FePc. The experimental value is of the same order of magnitude as the theoretical estimation from Eq. 4, although somewhat lower. Of course, Eq. 4 is just a rough approximation since the original model is derived for a fully occupied majority band, and a completely empty minority band, which is not our case, but it justifies qualitatively our finding of xy anisotropy in FePc.

5 Conclusions

The impact of Giulio Racah's work on magnetism cannot be overvalued and indeed, it is well known since decades. The recent development of third-generation synchrotron radiation sources have allowed the establishment of element-specific magnetometries based on X-ray absorption and scattering. The proper use of Racah-Wigner algebra in molecules and solids not only allows the detailed understanding of the experimental spectra, but also led to the formulation, by Theo Thole and coworkers, of simple *sum rules* allowing the separate determination of orbital and spin magnetic moments. These late products of Racah's methods have had a great impact on today magnetism, as scientific literature continuously corroborates.

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References

[1] E.U. Condon and G.H. Shortley, “The Theory of Atomic Spectra” (Cambridge University Press, 1963).

[2] G. Racah, *Physical Review* **61**, 186 (1942).

[3] G. Racah, *Physical Review* **62**, 438 (1942).

[4] G. Racah, *Physical Review* **63**, 367 (1943).

[5] G. Racah, *Physical Review* **76**, 1352 (1949).

[6] H. Bethe, Annalen der Physik, 3, 135 (1929).

[7] Y. Tanabe and S. Sugano, Journal of the Physical Society of Japan 9, 753 (1954).

[8] Y. Tanabe and S. Sugano, Journal of the Physical Society of Japan 9, 766 (1954).

[9] Y. Tanabe and S. Sugano, Journal of the Physical Society of Japan 11, 864 (1956).

[10] Ch. Kittel, Introduction to solid state physics, 7th ed. (John Wiley & Sons Inc., New York, 1996).

[11] B.R. Judd, Phys. Rev. 127, 750 (1962).

[12] G.S. Ofelt, J. Chem. Phys. 37, 511 (1962).

[13] B. G. Wybourne, Spectroscopic Properties of Rare Earths (J. Wiley & Sons, Inc., New York, 1965).

[14] J. F. Herbst, Reviews of Modern Physics 63, 828 (1991).

[15] A.P. Yutsis, I.B. Levinson and V.V. Vanagas, Mathematical Apparatus of the Theory of Angular Momentum (Israel Program for Scientific Translation, Jerusalem, 1962).

[16] B. R. Judd, Second Quantization and Atomic Spectroscopy (Baltimore: Johns Hopkins)

[17] Robert D. Cowan, The Theory of Atomic Structure and Spectra; Los Alamos Series in Basic and Applied Sciences, vol. 3. University of California Press, Berkeley, 1981.

[18] http://www.tcd.ie/Physics/People/Cormac.McGuinness/Cowan/

[19] G. van der Laan, Lect. Notes Phys. 697, 143 (2006)

[20] H. Wende, Rep. Prog. Phys. 67, 2105 (2004).

[21] H. Dürr et al., IEEE Trans. on Magnetics 45, 15 (2009).

[22] J. Stöhr and H. C: Siegmann, Magnetism: from fundamentals to nanoscale dynamics, Springer Series in Solid-State Physics 152. (Springer-Verlag, Berlin Heidelberg 2006).

[23] G. Schütz et al., Phys. Rev. Lett. 58, 737 (1987).

[24] G. van der Laan, B. T. Thole, G. A. Sawatzky, J. B. Goedkoop, J. C. Fuggle, J.M. Esteva, R. Karnatak, J. P. Remeika, and H. A. Dabkowska, Phys. Rev. B 34, 6529 (1986)

[25] P. H. Butler, ”Point Group Symmetry, Applications, Methods and Tables (Plenum, New York, 1981).

[26] G. van der Laan, J. Electron Spectrosc. Rel. Phenom. 86, 41 (1997)

[27] G. van der Laan and B. T. Thole Phys. Rev. Lett. 60, 1977 (1988).

[28] B. T. Thole and G. van der Laan, Phys. Rev. A 38, 1943 (1988).

[29] J. Bartolomé, F. Bartolomé, L. M. García, E. Roduner, Y. Akdogan, F. Wilhelm, and A. Rogalev, Phys. Rev. B 80, 014404 (2009).

[30] K. T. Moore and G. van der Laan, Rev. Mod. Phys. 81, 235 (2009).

[31] J. L. Erskine and E. A. Stern, Physical Review B 12, 5016 (1975)

[32] B. T. Thole, P. Carra, F. Sette, G. van der Laan, Phys. Rev. Lett. 68 (1992) 1943.

[33] M. Altarelli, Phys. Rev. B 47, 597 (1993).

[34] P. Carra, B. T. Thole, M. Altarelli, X. Wang, Phys. Rev. Lett. 70 (1993) 694.

[35] J. Kanamori: in *Magnetism* edited by G. T. Rado and H. Suhl, Vol. 1, 189 (Acad. Press, 1963).

[36] P. Carra, M. Fabrizio, and B. T. Thole, Phys. Rev. Lett. 74, 3700 (1995).

[37] M. van Veenendaal, P. Carra, B. T. Thole. Phys. Rev. B 54, 16010 (1996)

[38] M.H. Krisch, C.C. Kao, F. Sette, W.A. Caliebe, K. Hmlinen, J.B. Hastings, Phys. Rev. Lett. 74, 4931 (1995).

[39] M. Krisch, F. Sette, U. Bergmann, C. Masciovecchio, R. Verbeni, J. Goulon, W. Caliebe, and C. C. Kao , Phys. Rev. B 54, R12673 (1996)

[40] F. Bartolomé, J.M. Tonnerre, L. Sève, D. Raoux, J. Chaboy, L.M. Garcia, M. Krisch, C.C. Kao, Phys. Rev. Lett. 79, 3775 (1997).

[41] G. van der Laan, J. Electron Spectr. Rel. Phenom.101103, 859 (1999).

[42] http://www.zyvex.com/nanotech/feynman.html

[43] X. Liu et al, Phys Rev Lett 97, 253401 (2006).

[44] S. K. Arora, et al., Phys. Rev. B 77, 134443 (2008), and IEEE Trans. Magn. 44, 2628 (2008)

[45] J. Orna et al. Phys. Rev. B 81, 144420 (2010).

[46] J. Bartolomé, F. Bartolomé, L.M. García, G. Filoti, T. Gredig, C.N. Colesniuc, I.K. Schuller, J.C. Cezar, Phys. Rev. B 81, 195405 (2010).

[47] P. Bruno, Phys. B 39, 865 (1989)

[48] G. van der Laan, J. Phys.: Condens. Matter 10, 3239 (1998).

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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 $\mathrm{Mo(CN)}_8^{4-}$ 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.

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 $SO(3) \to O$ 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

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

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

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

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

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

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

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

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

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

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

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

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

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

where the reduced matrix element $(\| \ldots \|)$ 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 $\int_G \dots dR$, which applies when G is a compact continuous group, should be understood as $\sum_{R\in G} \cdots$ 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

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

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

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

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–$a\alpha$)$_\rho$ 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

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

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 $(3\text{–}a\alpha)_\rho$ 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 $3\text{–}a\alpha$ 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 $3\text{–}a\alpha$ 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 $3\text{–}a\alpha$ 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 $3\text{–}a\alpha$ 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 $(3\text{–}a\alpha)_\rho$ symbol constitutes a generalization to the case of an arbitrary finite or compact group of the $3\text{–}jm$ 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:

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

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

and

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

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

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

and

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

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 $(\tau' a' \alpha' | T^b_\beta | \tau a \alpha)$ can be decomposed as

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

Alternatively, (62) can be cast into the form

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

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 $(3\text{–}a\alpha)_\rho$ 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 $(\tau'_a \tau'_b a' b' \rho' c' \gamma' | \{\mathbf{T}^d \otimes \mathbf{U}^e\}^{\sigma f}_{\varphi} | \tau_a \tau_b a b \rho c \gamma)$ 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 $(\tau' a' \alpha' | T^b_\beta | \tau a \alpha)$ 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 $(\tau' a' \alpha' | T^b_\beta | \tau a \alpha) \neq 0$, 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 $(a_1a_2\alpha_1\alpha_2|\rho a\alpha)$ CGC for the G_a group is replaced by the $(a_1a_2\alpha_1\Gamma_1\gamma_1\alpha_2\Gamma_2\gamma_2|\rho a\alpha\Gamma\gamma)$ 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

$$(a_1a_2\alpha_1\Gamma_1\gamma_1\alpha_2\Gamma_2\gamma_2|\rho a\alpha\Gamma\gamma) = \sum_\beta (\Gamma_1\Gamma_2\gamma_1\gamma_2|\beta\Gamma\gamma)(a_1\alpha_1\Gamma_1 + a_2\alpha_2\Gamma_2|\rho a\alpha\Gamma)_\beta \tag{66}$$

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 $(j_1j_2m_1m_2|jm)$. 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

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} := (2j_3+1)^{-\frac{1}{2}} (-1)^{j_3 - m_3 - 2j_2} (j_2j_1m_2m_1|j_3, -m_3) \tag{69}$$

provided we chose $M(j_2j_1, j_3) = (-1)^{2j_1}$. 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–j Wigner (or $\bar{W}$ Fano-Racah) symbol and the 9–j Wigner (or X Fano-Racah) symbol, respectively. More precisely, we have

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

and

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

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

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

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 $\{|\tau j a\Gamma\gamma) : \gamma \text{ ranging }\}$ is an ITS of vectors spanning the matrix representation D^{Γ} of G^* while $\{|\tau j a\Gamma\gamma) : a\Gamma\gamma \text{ ranging }\}$ 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 $\{T_{\gamma}^{(ka\Gamma)} : \gamma \text{ ranging }\}$ and $\{T_{a\Gamma\gamma}^{(k)} : a\Gamma\gamma \text{ ranging}\}$.

3 - Wigner-Eckart theorems

As an important consequence of the latter two remarks, we may apply the Wigner-Eckart theorem either for the group $SU(2)$ in a $SU(2) \supset G^*$ basis or for the group G^* in a $G^* \subset SU(2)$ basis. For G^* in a $G^* \subset SU(2)$ basis, (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

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

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 $2\text{–}a\alpha$ and $(3\text{–}a\alpha)_\rho$ 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 $1\text{–}ja\Gamma\gamma$ 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 $1\text{–}jm$ symbol is defined by (67) and (68). The $\bar{f}$ or $3\text{–}ja\Gamma\gamma$ symbol defined through

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

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 $1\text{–}ja\Gamma\gamma$ symbol reduce to the $3\text{–}jm$ Wigner symbol and to the $1\text{–}jm$ Herring-Wigner symbol, respectively. The $1\text{–}ja\Gamma\gamma$ and $\bar{f}$ symbols are thus $2\text{–}a\alpha$

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 $(3\text{–}\Gamma\gamma)_\rho$ according to

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

where the $\bar{f}((\ldots))$ 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

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

(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 $(3\text{–}a\alpha)_\rho$ 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

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

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 $j = \hat{\jmath}(\Gamma)$ for the representation matrices D^Γ.

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

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

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

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

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 $(-1)^{\hat{\jmath}_1(\Gamma_1)+\hat{\jmath}_2(\Gamma_2)+\hat{\jmath}_3(\Gamma_3)}$ 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

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

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

$$\begin{aligned} B_{00}: \quad & \phi(00;0) = \frac{1}{\sqrt{3}} (\phi_2 + \phi_1 + \phi_0) \\ & \phi(01;0) = \frac{1}{\sqrt{3}} \left(\phi_2 + q\phi_1 + q^2\phi_0\right) \\ & \phi(02;0) = \frac{1}{\sqrt{3}} \left(\phi_2 + q^2\phi_1 + q\phi_0\right) \end{aligned} \tag{136}$$

$$\begin{aligned} B_{01}: \quad & \phi(10;0) = \frac{1}{\sqrt{3}} (\phi_2 + q\phi_1 + q\phi_0) \\ & \phi(11;0) = \frac{1}{\sqrt{3}} \left(\phi_2 + q^2\phi_1 + \phi_0\right) \\ & \phi(12;0) = \frac{1}{\sqrt{3}} \left(\phi_2 + \phi_1 + q^2\phi_0\right) \end{aligned} \tag{137}$$

$$\begin{aligned} B_{02}: \quad & \phi(20;0) = \frac{1}{\sqrt{3}} \left(\phi_2 + q^2\phi_1 + q^2\phi_0\right) \\ & \phi(21;0) = \frac{1}{\sqrt{3}} (\phi_2 + \phi_1 + q\phi_0) \\ & \phi(22;0) = \frac{1}{\sqrt{3}} (\phi_2 + q\phi_1 + \phi_0) \end{aligned} \tag{138}$$

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.□

4.5.1 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

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

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

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

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

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

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.

(super)symmetries → chain of groups → invariance or
co-variance → 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, $\mathrm{AdS}_4/\mathrm{CFT}_3$, 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

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[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.

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References

[1] G. Racah, *Phys. Rev.* **61**, 186 (1942).

[2] G. Racah, *Phys. Rev.* **62**, 438 (1942).

[3] G. Racah, *Phys. Rev.* **63**, 367 (1943).

[4] G. Racah, *Phys. Rev.* **76**, 1352 (1949).

[5] G. Racah, Group Theory and Spectroscopy, Report CERN61-8 (CERN, Geneva, 1961).

[6] G. Racah, *Ergebnisse der exakten Naturwissenschaften* **37**, 27 (1965).

[7] U. Fano and G. Racah, "Irreducible Tensorial Sets" (Academic Press, New York, 1959).

[8] I. Talmi, *Nucl. Phys.* **83**, 1 (1966).

[9] B.R. Judd, "Operator Techniques in Atomic Spectroscopy" (McGraw-Hill, New York, 1963).

[10] B.G. Wybourne, "Spectroscopic Properties of Rare Earths" (John Wiley, New York, 1965).

[11] E.U. Condon and H. Odabaşi, "Atomic Structure" (Cambridge University Press, Cambridge, 1980).

[12] A. de-Shalit and I. Talmi, "Nuclear Shell Theory" (Academic, New York, 1963).

[13] F. Iachello and A. Arima, "The Interacting Boson Model" (Cambridge University Press, Cambridge, 1987).

[14] A. Frank and P. Van Isacker, "Algebraic Methods in Molecular and Nuclear Structure Physics" (John Wiley, New York, 1994).

[15] P. Van Isacker, *Rep. Prog. Phys.* **62**, 1661 (1999).

[16] A. Frank, J. Jolie and P. Van Isacker, "Symmetries in Atomic Nuclei: From Isospin to Supersymmetry" (Springer, Berlin, 2009).

[17] G. Racah, *J. Chem. Phys.* **11**, 214 (1943).

[18] W. Low, The optical and ESR spectrum of Yb(IV) in the cubic crystal field, in: "Spectroscopic and Group Theoretical Methods in Physics, Racah Memorial Volume", eds. F. Bloch, S.G. Cohen, A. de-Shalit, S. Sambursky and I. Talmi (North-Holland, Amsterdam, 1968).

[19] W. Low, Optical spectra of paramagnetic solids, in: "Quantum Electronics", ed. C.H. Townes (Columbia University Press, New York, 1960).

[20] W. Low, Optical spectra of paramagnetic solids, in: "Advances in Quantum Electronics", ed. J.R. Singer (Columbia University Press, New York, 1961).

[21] G. Schoenfeld, M.Sc. thesis (The Hebrew University, Jerusalem, 1959).

[22] W. Low and G. Rosengarten, *J. Molec. Spectrosc.* **12**, 319 (1964).

[23] M. Flato, M.Sc. thesis (The Hebrew University, Jerusalem, 1960).

[24] M. Flato, *J. Molec. Spectrosc.* **17**, 300 (1965).

[25] M. Kibler, The master thesis of Moshé Flato, in: "Conférence Moshé Flato 1999", Vol. II, eds. G. Dito and D. Sternheimer (Kluwer, Dordrecht, 2000).

[26] M. Kibler, *J. Molec. Spectrosc.* **26**, 111 (1968).

[27] M. Kibler, *Int. J. Quantum Chem.* **3**, 795 (1969).

[28] M. Kibler, *C.R. Acad. Sci. (Paris) B* **268**, 1221 (1969).

[29] H.A. Bethe, *Ann. Physik* **3**, 133 (1929).

[30] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan* **9**, 753 (1954).

[31] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan* **9**, 766 (1954).

[32] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan* **11**, 864 (1956).

[33] Y. Tanabe and H. Kamimura, *J. Phys. Soc. Japan* **13**, 394 (1958).

[34] S. Sugano and Y. Tanabe, *J. Phys. Soc. Japan* **13**, 880 (1958).

[35] S. Sugano, Y. Tanabe and H. Kamimura, "Multiplets of Transition-Metal Ions in Crystals" (Academic, New York, 1970).

[36] J.S. Griffith, *Trans. Faraday Soc.* **54**, 1109 (1958).

[37] J.S. Griffith, *Trans. Faraday Soc.* **56**, 193 (1960).

[38] J.S. Griffith, *Trans. Faraday Soc.* **56**, 996 (1960).

[39] J.S. Griffith, *Molec. Phys.* **3**, 79 (1960).

[40] J.S. Griffith, *Molec. Phys.* **3**, 285 (1960).

[41] J.S. Griffith, *Molec. Phys.* **3**, 457 (1960).

[42] J.S. Griffith, *Molec. Phys.* **3**, 477 (1960).

[43] J.S. Griffith, *Molec. Phys.* **5**, 503 (1963).

[44] J.S. Griffith, "The Theory of Transition-Metal Ions" (Cambridge University Press, Cambridge, 1961).

[45] J.S. Griffith, "The Irreducible Tensor Method for Molecular Symmetry Groups" (Prentice-Hall, Englewood Cliffs, 1962).

[46] Tang Au-chin, Sun Chia-chung, Kiang Yuan-sun, Deng Zung-hau, Liu Jo-chuang, Chang Chian-er, Yan Go-sen, Goo Zien and Tai Shu-shan, *Sci. Sinica (Peking)* **15**, 610 (1966).

[47] Tang Au-chin, Sun Chia-chung, Kiang Yuan-sun, Deng Zung-hau, Liu Jo-chuang, Chang Chain-er, Yan Guo-sen, Goo Zien and Tai Shu-shan, "Theoretical Method of the Ligand Field Theory" (Science Press, Peking, 1979).

[48] Tang Au-chin, Sun Chia-chung and Li Bei-foo, *Int. J. Quantum Chem.* **18**, 545 (1980).

[49] Au-chin Tang, Chia-chung Sun and Bei-foo Li, *Int. J. Quantum Chem. Quantum Chem. Symp.* **14**, 521 (1980).

[50] Chia-chung Sun, Yan-de Han, Be-fu Li and Qian-shu Li, *Int. J. Quantum Chem.* **23**, 169 (1983).

[51] D.T. Sviridov and Yu.F. Smirnov, *Sov. Phys. Dokl.* **13**, 565 (1968).

[52] C.V. Vonsovski, C.V. Grimailov, V.I. Tcherepanov, A.N. Meng, D.T. Sviridov, Yu.F. Smirnov and A.E. Nikiforov, "Crystal-Field Theory and Optical Spectra of Partly Filled d Shell Transition Ions" (Nauka, Moscow, 1969).

[53] D.T. Sviridov, Yu.F. Smirnov and V.N. Tolstoy, in: "Spektroskopiya kristallov" (Nauka, Moscow, 1975).

[54] D.T. Sviridov, R.K. Sviridova and Yu.F. Smirnov, "Optical Spectra of Transition-Metal Ions in Crystal" (Nauka, Moscow, 1976).

[55] D.T. Sviridov and Yu.F. Smirnov, “Teoriya opticheskikh spektrov perekhodnykh metallov” (Nauka, Moscow, 1977).

[56] M. Kibler and G. Grenet, *Int. J. Quantum Chem.* **28**, 213 (1985).

[57] M. Kibler and G. Grenet, *Int. J. Quantum Chem.* **29**, 11 (1986).

[58] M. Kibler and G. Grenet, *Int. J. Quantum Chem.* **29**, 485 (1986).

[59] M. Kibler and J.-C. Gâcon, *Croat. Chem. Acta* **62**, 783 (1989).

[60] M.R. Kibler, Finite symmetry adaptation in spectroscopy, in: “Recent Advances in Group Theory and Their Application to Spectroscopy”, ed. J.C. Donini (Plenum, New York, 1979).

[61] M.L. Ellzey, Jr., *Int. J. Quantum Chem.* **7**, 253 (1973).

[62] E. König and S. Kremer, *Z. Naturforsch.* **29a**, 1179 (1974).

[63] P. Rudra and M.K. Sikdar, *J. Phys. C: Solid State Phys.* **10**, 75 (1977).

[64] B. Lulek, T. Lulek and B. Szcepaniak, *Acta Phys. Polon. A* **54**, 545 (1978).

[65] P.H. Butler and M.F. Reid, *J. Phys. A: Math. Gen.* **12**, 1655 (1979).

[66] J.D. Newmarch and R.M. Golding, *J. Math. Phys.* **22**, 233 (1981).

[67] M. Błaszak, *phys. status solidi (b)* **109**, 195 (1982).

[68] R. Conte and J. Raynal, *J. Math. Phys.* **26**, 2413 (1985).

[69] S. Cesare and V. Del Duca, *Riv. Nuovo Cimento* **10**, 1 (1987).

[70] J. Moret-Bailly, *J. Molec. Spectrosc.* **15**, 344 (1965).

[71] J.P. Champion, G. Pierre, F. Michelot and J. Moret-Bailly, *Can. J. Phys.* **55**, 512 (1977).

[72] V. Boudon and F. Michelot, *J. Molec. Spectrosc.* **165**, 554 (1994).

[73] V. Boudon, F. Michelot and J. Moret-Bailly, *J. Molec. Spectrosc.* **166**, 449 (1994).

[74] J. Patera and P. Winternitz, *J. Math. Phys.* **14**, 1130 (1973).

[75] J. Patera and P. Winternitz, *J. Chem. Phys.* **65**, 2725 (1976).

[76] C.W. Nielson and G.F. Koster, “Spectroscopic Coefficients for the p^n, d^n and f^n Configurations” (Technology Press, Cambridge, 1963).

[77] K. Rajnak and B.G. Wybourne, *J. Chem. Phys.* **41**, 565 (1964).

[78] C.K. Jørgensen, “Modern Aspects of Ligand Field Theory” (North-Holland, Amsterdam, 1971).

[79] M. Kibler, *Int. J. Quantum Chem.* **9**, 403 (1975).

[80] D.J. Newman, *Adv. Phys.* **20**, 197 (1971).

[81] B.D. Bird, E.A. Cooke, P. Day and A.F. Orchard, *Phil. Trans. Roy. Soc. A* **276**, 277 (1974).

[82] L. Pueyo and J.W. Richardson, *J. Chem. Phys.* **67**, 3583 (1977).

[83] C. Daul and P. Day, *Molec. Phys.* **34**, 1707 (1977).

[84] J. Weber and C. Daul, *Molec. Phys.* **39**, 1001 (1980).

[85] B.R. Judd, *Phys. Rev.* **127**, 750 (1962).

[86] G.S. Ofelt, *J. Chem. Phys.* **37**, 511 (1962).

[87] T.R. Bader and A. Gold, *Phys. Rev.* **171**, 997 (1968).

[88] M. Kibler and M. Daoud, *Lett. Math. Phys.* **28**, 269 (1993).

[89] M. Daoud and M. Kibler, *Phys. Rev. B* **52**, 12667 (1995).

[90] P.A. Cox, *Struc. Bonding* **24**, 59 (1975).

[91] G. Grenet, Y. Jugnet, Tran Minh Duc and M. Kibler, *Chem. Phys. Lett.* **62**, 125 (1979).

[92] G. Grenet, Y. Jugnet, Tran Minh Duc and M. Kibler, *J. Chem. Phys.* **72**, 218 (1980).

[93] G. Grenet, Y. Jugnet, Tran Minh Duc and M. Kibler, *J. Chem. Phys.* **74**, 2163 (1981).

[94] G. Grenet, Y. Jugnet, Tran Minh Duc and M. Kibler, *Phys. Rev. B* **24**, 2349 (1981).

[95] L.C. Biedenharn and J.D. Louck, Angular momentum in quantum physics, in: "Encyclopedia of Mathematics and Its Applications", Vol. 8, ed. G.-C. Rota (Cambridge University Press, Cambridge, 1985).

[96] L.C. Biedenharn and J.D. Louck, The Racah-Wigner algebra in quantum theory, in: "Encyclopedia of Mathematics and Its Applications", Vol. 9, ed. G.-C. Rota (Cambridge University Press, Cambridge, 1985).

[97] M. Kibler and G. Grenet, *J. Math. Phys.* **21**, 422 (1980).

[98] E.P. Wigner, *Am. J. Math.* **63**, 57 (1941).

[99] E.P. Wigner, On the matrices which reduce the Kronecker products of representations of S.R. groups, manuscript from 1940 published in: "Quantum Theory of Angular Momentum", eds. L.C. Biedenharn and H. van Dam (Academic, New York, 1965).

[100] E.P. Wigner, Condition that the irreducible representations of a group considered as representations of a subgroup do not contain any representation of the subgroup more than once, in: "Spectroscopic and Group Theoretical Methods in Physics, Racah Memorial Volume", eds. F. Bloch, S.G. Cohen, A. de-Shalit, S. Sambursky and I. Talmi (North-Holland, Amsterdam, 1968).

[101] W.T. Sharp, Racah algebra and the contraction of groups, Report AECL-1098 (Atomic Energy of Canada Ltd, Chalk River, 1960).

[102] J.R. Derome and W.T. Sharp, *J. Math. Phys.* **6**, 1584 (1965).

[103] J.R. Derome, *J. Math. Phys.* **7**, 612 (1966).

[104] P.H. Butler, *Phil. Trans. Roy. Soc. A* **277**, 545 (1975).

[105] G.F. Koster, J.O. Dimmock, R.G. Wheeler and H. Statz, "Properties of the Thirty-two Point Groups" (M.I.T. press, Mass., 1963).

[106] M.R. Kibler, *J. Phys. A: Math. Gen.* **10**, 2041 (1977).

[107] C. Eckart, *Rev. Mod. Phys.* **2**, 305 (1930).

[108] E.P. Wigner, "Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren" (Vieweg, Braunschweig, 1931).

[109] M.R. Kibler, *Int. J. Quantum Chem.* **23**, 115 (1983).

[110] A.R. Edmonds, "Angular Momentum in Quantum Mechanics" (Princeton University Press, Princeton, 1960).

[111] M. Balevičius and A. Bolotin, *Liet. Fiz. Rinkinys.* **4**, 67 (1964).

[112] A. Jucys and A. Bandzaitis, "Theory of Angular Momentum in Quantum Mechanics" (Mintis, Vilnius, 1965).

[113] V.K. Agrawala and J.G. Belinfante, *Ann. Phys. (N.Y.)* **49**, 130 (1968).

[114] G.E. Stedman, *J. Phys. A: Math. Gen.* **8**, 1021 (1975).

[115] M. Kibler and E. Elbaz, *Int. J. Quantum Chem.* **16**, 1161 (1979).

[116] L.C. Biedenharn and M.A. Lohe, "Quantum Group Symmetry and q-Tensor Algebras" (World Scientific, Singapore, 1995).

[117] Yu.F. Smirnov, V.N. Tolstoĭ and Yu.I. Kharitonov, *Soviet J. Nuclear Phys.* **56**, 690 (1993).

[118] M.R. Kibler, R.M. Asherova and Yu.F. Smirnov, "Some aspects of q- and qp-boson calculus", in: Symmetries in Science VIII, ed. B. Gruber (Plenum Press, New York, 1995).

[119] R.M. Asherova and Yu.F. Smirnov and V.N. Tolstoy, *Phys. Atomic Nuclei* **64**, 2080 (2001).

[120] M.R. Kibler, *Collect. Czech. Chem. Commun.* **70**, 771 (2005).

[121] I.D. Ivanović, *J. Phys. A: Math. Gen.* **14**, 3241 (1981).

[122] W.K. Wootters and B.D. Fields, *Ann. Phys. (N.Y.)* **191**, 363 (1989).

[123] A.R. Calderbank, P.J. Cameron, W.M. Kantor and J.J. Seidel, *Proc. London Math. Soc.* **75**, 436 (1997).

[124] M.R. Kibler, *Int. J. Mod. Phys. B* **20**, 1792 (2006).

[125] M.R. Kibler and M. Planat, *Int. J. Mod. Phys. B* **20**, 1802 (2006).

[126] O. Albouy and M.R. Kibler, *SIGMA* **3**, 076 (2007).

[127] M.R. Kibler, *J. Phys. A: Math. Theor.* **41**, 375302 (2008).

[128] M.R. Kibler, *J. Phys. A: Math. Theor.* **42**, 353001 (2009).

[129] B.C. Berndt, R.J. Evans and K.S. Williams, "Gauss and Jacobi Sums" (Wiley, New York, 1998).

[130] H. Weyl, "The Theory of Groups and Quantum Mechanics" (Dover, New York, 1931).

[131] S. Bandyopadhyay, P.O. Boykin, V. Roychowdhury and F. Vatan, *Algorithmica* **34**, 512 (2002).

[132] J. Lawrence, Č. Brukner and A. Zeilinger, *Phys. Rev. A* **65**, 032320 (2002).

[133] A.O. Pittenger and M.H. Rubin, *J. Phys. A: Math. Gen.* **38**, 6005 (2005).

[134] P. Šťovíček and J. Tolar, *Rep. Math. Phys.* **20**, 157 (1984).

[135] R. Balian and C. Itzykson, *C. R. Acad. Sci. (Paris)* **303**, 773 (1986).

[136] J. Patera and H. Zassenhaus, *J. Math. Phys.* **29**, 665 (1988).

[137] I. Bengtsson, *Preprint* quant-ph/0610216 (2006).

[138] P.O. Boykin, M. Sitharam, P.H. Tiep and P. Wocjan, *Quantum Inf. Comput.* **7**, 371 (2007).

[139] M.R. Kibler, *Int. J. Quantum Chem.* **9**, 421 (1975).

[140] M. Kibler and J. Katriel, *Phys. Lett. A* **147**, 417 (1990).

[141] M. Kibler and A. Partensky, Question on an alternative parametrization for the theory of complex spectra, in: "Symmetry and Structural Properties of Condensed Matter", eds. W. Florek, T. Lulek and M. Mucha (World Scientific, Singapore, 1991).

[142] O. Laporte and J.R. Platt, *Phys. Rev.* **62**, 305 (1942).

[143] R.B. King, *Molec. Phys.* **104**, 1855 (2006).

[144] W. Ehlert, *Zeitschr. Physik* **51**, 6 (1928).

[145] E.P. Wigner, *Phys. Rev.* **51**, 105 (1937).

[146] L.J. Boya and R. Campoamor-Stursberg, *J. Phys. A: Math. Theor.* **42**, 235203 (2009).

[147] E.P. Wigner, *Z. Physik* **43**, 624 (1927).

[148] A.O. Barut, Group structure of the periodic system, in: “The Structure of Matter”, ed. B.G. Wybourne (Univ. of Canterbury Publications, New Zealand, 1972).

[149] Yu.B. Rumer and A.I. Fet, *Theor. Math. Phys.* **9**, 1081 (1972).

[150] M.R. Kibler, *Molec. Phys.* **102**, 1221 (2004).

[151] N. Zeldes, *Arch. Hist. Exact Sci.* **63**, 289 (2009).

[152] Conférence Moshé Flato 1999 (`http://monge.u-bourgogne.fr/cmf/cmf1999/toc1999.html`). The proceedings of the Conférence Moshé Flato 1999 were published by Kluwer Academic Publishers in the series Mathematical Physics Studies in July 2000. They are constituted of 2 volumes (x+428 pages and vi+348 pages) and are edited by Giuseppe Dito and Daniel Sternheimer. See also the links to Moshé Flato Conferences and Lecture Series (`http://www.math.bgu.ac.il/events/flato/2011-Flato-Lectures.html`).

[153] Moshé Flato - Personal Recollections, *Lett. Math. Phys.* **48**, 5 (1999), (`http://www.springerlink.com/content/l8458j67uk557514/`).