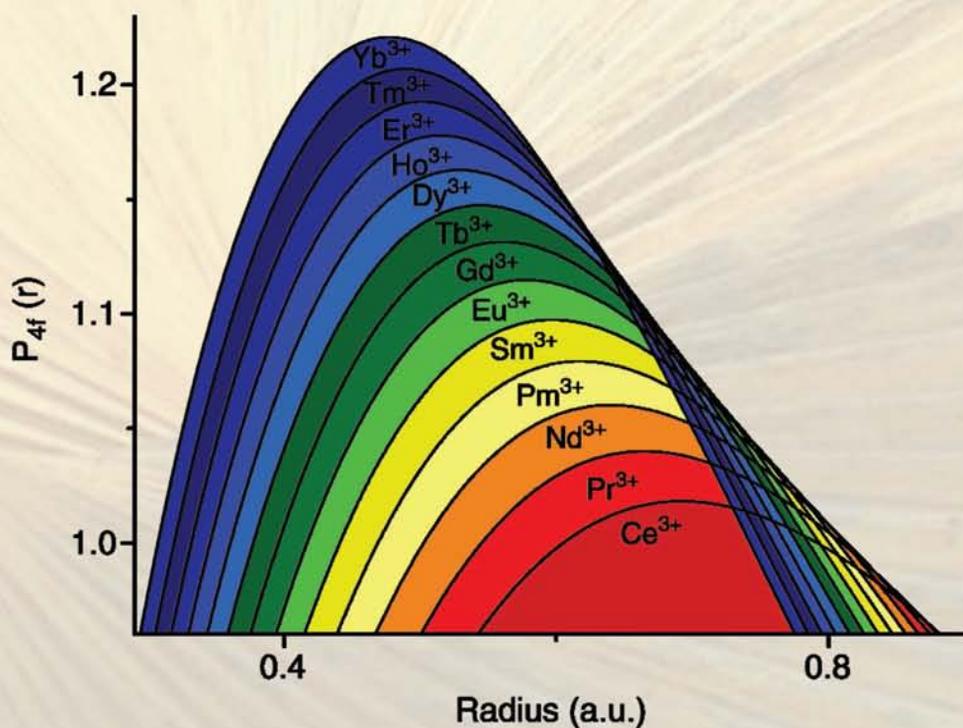


OPTICAL SPECTROSCOPY OF LANTHANIDES

Magnetic and Hyperfine Interactions



Brian G. Wybourne and Lidia Smentek

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Foreword

*Memories are a gift of the past,
That we hold in the present,
To create what can be a great future.
Treasure and keep memories,
For the sake of Life.*

Mattie J. T. Stepanek, from “About Memories” (Hyperion/VSP, 2002)

This book is a result of an unplanned project which has been ruled by fate. Neither Brian Wybourne nor I were even thinking about writing a book. Being deeply involved in day-after-day fascinating research, we simply did not have time. There was no time to slow down, collect thoughts and results of our investigations, and to prepare the manuscript, since too many revolutionary and novel materials, properties and applications were continuously brought to the light, not only in the spectroscopy of lanthanides, the field of our research. For 13 years of our friendship and collaboration in the Physics Department, Nicolaus Copernicus University in Toruń, Poland, we were suggesting to each other to write a book, just teasing and treating this idea only as a joke, since we both realized the size of such a task and the nature of its responsibility. Brian knew this as an experienced author, who published his first book when I was still in high school, and I, without any experience, having been only the editor of special issues of scientific journals, was simply overwhelmed by such a project and even afraid to think about it.

2003 was very difficult year for me. I was a fresh cancer survivor who was trying to recover after my health crisis to gain the strength to go through a long and painful procedure of a promotion in my native institute. Unfortunately the procedure was based on the old-fashioned judgment of a “woman in physics” rather than on the evaluation of the scientific achievements of a physicist, and eventually I was denied promotion. Brian suffered with me, trying to give me all possible support. Being saved several times from health breakdowns, and being blessed in my life to be a scientist not for recognition but for the sake of fascination of my research, I have survived the final decision of my colleagues simply by focusing on my work. But I was crushed at the beginning of 2003, when my mother passed away after almost two years of struggles. My world shrank to the size of a dot. As the best therapy for my sorrow I started to teach at Vanderbilt University in Nashville (I have held an appointment in the Department of Chemistry since 1994) where a group of very talented, hard working and nice students from the Graduate School of the Physics Department helped me to go through the toughest time.

From Nashville I was keeping vivid contact with Brian Wybourne, and thanks to e-mail we were able to discuss science, exchange results and opinions, share the joy of teaching and also talk about our students. However I must admit that very often I

was missing just chatting with Brian, the atmosphere of which cannot be reproduced by any electronic medium.

The first week of November 2003 I spent in Toruń to follow the Polish tradition of celebrating All Saints Day and the Day of the Dead. Because of this special holiday there was not enough time to go through all the interesting subjects and issues with Brian that we had kept for some months to talk about directly. After my return to Nashville I received an e-mail message from Brian, which was his reply to my question about the elegance of his lecture notes we discussed while in Toruń. Brian's letter was a reaction to the joke I made, that in spite of the promises he had given to himself, it looks as though he was getting ready to write a monograph.

Dear Lidia,

Pleased to know you managed to download the notes - I thought you might have trouble with postscript. I have no plans to publish - I attached the copyright symbol to avoid [some colleagues]! I prepared the notes for my class but Andrzej (?) was the only survivor. He has been good at going through them and finding corrections hence I also gave him a complete copy. To complete the notes we need radial integrals etc to give some examples - not my forte! As a result the notes are left hanging. I don't think I have the energy to bring the notes to a publishable form. For that I would need a young dynamic collaborator who could knock them into shape. I understand that there is a person called Smentek who would fit the role and would, of course, become the first author. Maybe KBN could support such a project?

Regards Brian

I have to explain that the student mentioned in this letter (his name is misspelt above, which is not difficult to do for a foreigner) is my graduate student. This is Andrzej Kędziorowski, whom I left going to Nashville under the wings, guidance and care of one of the founders of the field of spectroscopy of rare earths, the outstanding and widely known Professor Brian Wybourne.

The tone of Brian's letter made me nervous especially when realizing that possibly we were approaching a dangerous point of talking seriously about writing a monograph. Being called to the blackboard by the Master, when the first astonishment went away, I was trying to imagine what it would have meant if we had indeed decided to write a book. We had co-authored several papers, we had spent hours on discussions, explaining to each other various issues and also arguing with each other. I knew that due to Brian's extensive knowledge and calm personality, writing a monograph with him would be not only a creative activity, but also it would provide pleasure and satisfaction. At the same time however I remembered so well Brian's negative attitude to writing a long manuscript and all the worries about problems he was aware of as a former author of several books. In order not to despair I was repeating to myself that it must be a joke....

It was not a joke. When I received the next e-mail message, I sensed that the idea had become a serious matter, but still the plan had all the aspects of a project for the future. At that moment in fact I was planning to go back to Toruń for an extended period of time, if my health would permit, and this move would make it easier to work together, if the decision was really made. Brian wrote:

Subj: Re: It is not easy....

Date: 11/12/03 9:21:04 AM Central Standard Time

From: bgw at phys.uni.torun.pl

To: mailto:Smentek1 at aol.com

Sent from the Internet (Details)

Dear Lidia,

I was pleased with Andrzej today. This morning he brought along two Masters students, one from Koepke and one from Wojtowicz, to my "lecture" on Spectro..... As Andrzej has up to today been the only student and I have simply taken the opportunity to talk with Andrzej I was totally unprepared. But it went well. I first got them to tell me what their thesis topics were, with Andrzej occasionally helping with English. One is working on Ce^{3+} and the other on energy transfer between Cr^{3+} and Nd^{3+} so we discussed the ground states of the ions - they didn't know the site symmetries so next week they are supposed to tell me. Anyhow it looks like next week I will discuss $3d^N$ and $4f^N$ and weak and strong crystal fields.

I didn't go to Jacek's group meeting though I did discuss some things with Jacek. I think his main thrust will be expecting everyone to compete for KBN grants etc with those who are producing being most favoured.

I said goodbye to Jacek as he was going to Warsaw after that to join Marta and fly to Katmandu.(...)

Unfortunately I did not have time to discuss a number of topics with Jacek. He had mentioned that KBN had a special fund for anyone writing a book. You mentioned Rudzikas's conference. I looked it up on the web. Unfortunately it was too late for me to discuss with Jacek. Possibly my KBN grant could cover your trip. However I need someone to check the status of my KBN grant. Clearly the grant must be totally expended by October next year.

I have no deadline for a completed manuscript. I had not thought of publishing until you raised the question. Maybe Springer Lecture Notes Series or locally like Physics as a Journey. I would expect to share authorship with my usual preference for alphabetical order. It would need a careful going through with you doing radial integrals etc etc. No rush. I'll see how I get on with the new students.

—4C this morning. Two Christmas cakes finished and I can smell the bread cooking! Too cloudy on Saturday to see the Lunar eclipse. I don't know how Copernicus became interested in such things. Likewise I have not seen Aurora Borealis which I understand was even seen in Florida!

Regards Brian

This was the last letter I received from Brian, ever; he was struck down by a stroke, and after ten days he passed away on November 26, 2003. These letters are like Brian's last will and testament left as instructions for what to do in the case of the worst. Therefore I did not have any choice but to start to think about the work which was dropped on my shoulders by fate. I wanted to be able to say what A. Einstein has said: "Now he has departed from this strange world a little ahead of me. That means nothing. People like us, who believe in **physics**, know that the distinction between past, present, and future is only a stubbornly persistent illusion"; but I could not.

Brian left me alone with the task of adopting his lecture notes to the form of a monograph, of deriving new expressions and calculating radial integrals to continue our research and extend the knowledge about the f-electron systems, of deriving conclusions and presenting the future prospects of our field. I am left alone with the responsibility for a **BOOK**, we agreed to work on together...It is difficult, but *“Obstacles cannot crush me. Every obstacle yields to stern resolve. He who is fixed to a star does not change his mind”* (Leonardo da Vinci).

Here I am presenting a completed project, our book, hoping that Brian would be proud of it.

Since 2003 Andrzej has developed his skills and has performed interesting investigations that hopefully will be collected soon as his PhD thesis. Unfortunately, there is no Professor Wybourne around to advise, criticize, help with English and, most of all, judge the scientific merit of his work. Instead, in order to have a closure of Andrzej's lucky chapter of the beginning of his career, when he was given a chance to learn from a famous Professor about the beauty and the secrets of Nature, I am presenting here some results of his work. The numerical results and graphical illustration of the developed formalism that are presented in chapter 21 is a report we both, Andrzej and I, owe to Brian.

In the letters presented here Brian mentioned the possibility of getting financial support from the Science Foundation of Poland (KBN) for the project of writing a monograph; I did not apply for this aid. Instead I was awarded a one year stipend from the Nicolaus Copernicus University in Toruń which I would like to acknowledge. The financial aspect was not so important as the acceptance of my project that was granted by the authorities of the University together with the stipend; I do appreciate this moral support.

During the 13 years Brian lived in Toruń we shared professional and personal experiences. Those gained by him in his native New Zealand and exotic Poland; and my own, which I gained in my native Poland where I live with the imagination about exotic New Zealand. And today, on Brian's birthday, when I am facing a challenge of presenting the results of my work to a wide audience, I can hear his voice quoting Victoria Holt:

“Never regret. If it's good, it's wonderful. If it's bad, it's experience”.

If so, having a positive attitude to the result of my mission, that is created by these words, I may follow the advice of Leonardo da Vinci:

“Every now and then go away, have a little relaxation, for when you come back to your work your judgment will be surer since to remain constantly at work will cause you to lose power of judgment. Go some distance away because then the work appears smaller, and more of it can be taken in at a glance, and a lack of harmony or portion is more readily seen”.

Lidia Smentek
March 5th, 2006

Preface

The monograph is devoted to the theoretical description of the spectroscopic properties of the rare earth ions doped in various materials. These systems revolutionize modern science and technology at all possible scales, *nano, micro and macro*. The tensor operators and the concepts of the Racah algebra are the language of the presentation. The level of complexity in the course of this monograph begins with the basic knowledge of the theory of nuclei and theory of angular momentum, develops through the standard description of the fine and magnetic hyperfine interactions, and their impact upon the energy structure of the lanthanide ions, to culminate in the advanced description of $f \longleftrightarrow f$ electric and magnetic dipole transitions, including sensitized luminescence and its application in the detection and treatment of cancer in various tissues.

The standard description is understood as a model in which the interactions via a certain physical mechanism are limited to those within the $4f$ shell. The extension of the approach, which is analyzed through the book in the case of various physical interactions, includes the inter-shell interactions. The inclusion of the perturbing impact of the excited configurations breaks the limitations of the single configuration approximation. It leads very often not only to a better accuracy of the theoretical model, but also introduces new selection rules, which shed new light upon the understanding of the observed phenomena.

Thanks to the screening of the electrons of the optically active $4f$ shell by the closed shells of the $5s$ and $5p$ symmetry, the theory of the spectroscopic properties of the lanthanides in crystals is based on perturbation theory. In practical applications, the zeroth order problem describes the free ion within the single configuration approximation. The influence of important physical mechanisms upon the energy or the transition probability is included in a perturbative way taking into account corrections to the wave functions caused by various perturbations. The list of the perturbing operators included in the theoretical approaches presented in the monograph contains the crystal field potential, electron correlation effects, spin-orbit interaction and magnetic and electric multipole hyperfine interactions. In order to extend this list of various interactions, which are in most cases limited to interactions within the orbital space, an effectively relativistic model of various transitions is also presented.

Almost half of the book evolved from lectures prepared by Brian G. Wybourne for the graduate students of the Institute of Physics, Nicolaus Copernicus University in Toruń, Poland in 2002/2003. Wherever possible, the lecture format of presentation is kept (although the monograph is not prepared as a textbook). Therefore useful MAPLE routines are provided, several derivations of new expressions are presented and supported by numerical results, and some of the chapters are concluded by additional problems left for the reader to exercise. The advanced level of the course addressed to graduate students is elevated by the discussion of the results presented in the second part of the book; these results were not published previously. Among these new issues of the optical spectroscopy of lanthanides in various materials are the hyperfine induced $f \longleftrightarrow f$ electric dipole transitions. In their description the

forcing role of the crystal field potential of the standard Judd-Ofelt theory is played by the electric dipole hyperfine interactions. This new source of contributions to the transition amplitude provides a potential explanation of the hypersensitivity of some electric dipole transitions to the environment. This is the property that causes serious problems with the theoretical reproduction of the intensities, when based on the standard parametrization of f -spectra. As a consequence of this discussion, and also as a result of the analysis of the relativistic approach to the $f \longleftrightarrow f$ transitions, a new parametrization scheme is introduced. Namely, in order to include all possibly important physical interactions within the spin-orbital space when using the fitting procedure, the unit tensor operators of the Judd-Ofelt theory are replaced by the double tensor operators.

The chapter devoted to the radial integrals is unique in the sense that its contents may not be found in the literature of the field. This chapter is mainly addressed to all those who are interested in the direct calculations of the amplitude of the $f \longleftrightarrow f$ transitions. For this purpose the values of all radial integrals of the theory of f -spectra are presented for all lanthanide ions. They are evaluated within the perturbed function approach, due to which a complete radial basis sets of one electron functions of given symmetry are taken into account. The tables include the radial integrals of the Judd-Ofelt effective operators, their values modified by the electron correlation effects taken into account at the third order, as well as those associated with the effective operators originating from intra-shell and inter-shell interactions via the spin-orbit and hyperfine interactions.

As an illustration of the formalism developed throughout the monograph to describe the subtleties of the electronic structure of lanthanide ions, its very attractive and promising application is presented in the last chapter. The particular case of sensitized luminescence of the organic chelates with the lanthanide ion placed in the center of the cage that are the tissue selective markers of the cancerous cells are described. The architecture of the cage, its symmetry, and in turn, their impact upon the efficiency of the energy transfer and consequently the luminescence, require theoretical techniques developed and presented in the monograph. To construct adequate and reliable theoretical models, and through them to gain the understanding of the physical reality of these materials, is a challenging task. This research is also important in the light of existing strong demand for non-invasive diagnostic aids for early detection of cancer and for powerful tools to cure the attacked tissue.

I hope that the reader finds the presentation clear and the discussion interesting and useful for further research devoted to the lanthanides and their amazing properties.

Lidia Smentek

About the Authors

Brian Garner Wybourne, a fellow of the Royal Society of New Zealand, was an outstanding physicist. A native of New Zealand, he was widely recognized throughout the scientific world. Just after completing his PhD at the University of Canterbury in Christchurch, New Zealand, he moved in 1960 to Johns Hopkins University in Baltimore. In 1963 he continued his research at Argonne National Laboratory. Three years later he returned to his home country as the youngest professor of physics ever appointed to a chair of the Physics Department of Canterbury University in Christchurch, to become its Head in 1982, until 1989. In 1991 he arrived in Toruń, Poland, as a Visiting Professor at the Institute of Physics, Nicolaus Copernicus University, and he stayed there for 13 years teaching, doing research, collaborating with many in the world, and enjoying the gothic architecture of the medieval town, the birthplace of Copernicus. He died on November 26, 2003 leaving a rich legacy to fellow-physicists and mathematicians, as well as to all *secular* people who are honest, ready to accept the diversities of the world, and are tolerant of all differences.

His interests were broad and deep. On his still existing personal web page he classified the fields of his research: “Generally: applications of symmetry in physics. Specifically: spectroscopic properties of lanthanides and actinides, mathematical and physical applications of Lie groups, theory of symmetric functions, computing properties of groups, interacting boson model of nuclei, mesoscopic and many-body systems”.

Brian G. Wybourne is the author of five books and of almost 190 scientific papers published in the best journals in the world. He is one of the pioneers and successful founders of the spectroscopy of rare earths. At the age of 30 he wrote the famous *Spectroscopic Properties of Rare Earths* (Wiley-Interscience, 1965), and then, almost every five years, a new book appeared, namely *Symmetry Principles and Atomic Spectroscopy* (Wiley-Interscience, 1970) and *Classical Groups for Physicists* (Wiley-Interscience, 1974).

Lidia Smentek is a physicist. Educated at Nicolaus Copernicus University in Toruń, Poland, she became a faculty member of the Institute of Physics just after graduation in 1971, and since 1994 is a professor of chemistry at Vanderbilt University, Nashville, Tennessee. She had the privilege to collaborate with Brian Wybourne, and the pleasure of being his friend. She is the author of about 80 scientific papers, the majority of which is devoted to the theory of f-spectra and unique ab-initio type numerical calculations performed for various spectroscopic properties of lanthanides. Recently she participates in the inter-disciplinary research (funded by NSF) on the tissue selective organic chelates containing the lanthanide ions, which are being designed as probes for detection of cancer. In the past she has served as a guest editor of special issues of *Molecular Physics* (three times) and *International Journal of Quantum Chemistry*. In 2005 she edited a book, Brian Garner Wybourne; *Memories and Memoirs* (Adam Marszałek Pub., 2005), to commemorate Brian’s scientific achievements and personal impact he had upon many in various places in the world.

1 Basic Facts of Nuclei

... when he imagined his education was completed, it had in fact not commenced; and that, although he had been at a public school and a university, he in fact knew nothing. To be conscious that you are ignorant is a great step to knowledge.

Benjamin Disraeli, *Sybil or The Two Nations* (1844)

The concept of quantum degeneracy and its controlled lifting by magnetic and electric fields is perhaps the most technologically important and practical development of the past century. It has led to the development of lasers, NMR imaging, modern telecommunications, the realization of Bose-Einstein condensation, and the potential realization of quantum computing. These applications have required a detailed understanding of the quantum theory of angular momentum in all its manifestations, starting with the angular momentum of nuclear states, the angular momentum of electronic states and of the coupling of angular momentum of nuclear with electronic states.

1.1 NUCLEONS

The basic building blocks of nuclei (here we ignore the quark substructure of the nucleons) are neutrons and protons. Both are spin $\frac{1}{2}$ particles with positive intrinsic parity, i.e. $J_p = \frac{1}{2}^+$. Following Heisenberg¹, the proton and neutron can be regarded as different charge states of the *nucleon*. The respective masses are (we will generally put $c = 1$)

$$m_p = 938.3 \text{ MeV} \quad m_n = 939.6 \text{ MeV} \quad (1-1)$$

In free space the neutron is unstable with a half-life of $t_{1/2} = 614.6 \text{ s}$ whereas the proton appears to be stable with $t_{1/2} > 10^{33} \text{ y}$. Within the nucleus, as a consequence of the Pauli exclusion principle, the proton *and* the neutron are stable.

Remarkably, the proton *and* the neutron both possess magnetic moments.

$$\mu_p = 2.7928 \quad \mu_n = -1.9128 \quad (1-2)$$

where the units are the Bohr nuclear magneton defined as

$$\mu_{B_N} = \frac{e \hbar}{2m_p} \quad (1-3)$$

An *isotope* of an element X having Z protons (Z is the *atomic number*) and N neutrons will be designated as



where

$$A = N + Z \quad (1-4)$$

with A being the *nucleon number*.

The force between nucleons is, to a good approximation, charge independent and of a short range. Its origin is to be found in the quark model which we shall not explore here. The basic nuclear model we shall consider is the *nuclear shell model*. To a first approximation we can consider the nucleons as executing harmonic oscillations about the nuclear centre of mass and hence as nucleons in an isotropic 3-dimensional harmonic oscillator.

1.2 THE ISOTROPIC HARMONIC OSCILLATOR

Recall that the energy eigenvalues of a 3-dimensional isotropic harmonic oscillator potential containing a single particle are given by

$$E_n = (n + \frac{3}{2})\hbar\omega \quad n = 0, 1, 2, \dots \quad (1-5)$$

corresponding to an infinite series of equally spaced levels. The n -th level has an orbital degeneracy of

$$\frac{(n+1)(n+2)}{2} \quad (1-6)$$

These are precisely the dimensions of the symmetric irreducible representations $\{n\}$ of the special unitary group $SU(3)$. The n -th level is associated with orbitals having the angular momentum quantum number ℓ such that

$$\ell = n, n-2, \dots, \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad (1-7)$$

Given that the nucleons have *even* intrinsic parity the states associated with the n -th level are all of the *same* parity which is *even* or *odd* as n is *even* or *odd*. The nucleons have spin $\frac{1}{2}$ and hence each orbital ℓ has a spin-orbital degeneracy of $4\ell + 2$. It is common in nuclear physics to prefix the orbital quantum number with the number of nodes in the single particle wavefunction. Thus the orbitals associated with n -level are in the sequence

$$1s; 1p; 2s, 1d; 2p, 1f; 3s, 2d, 1g; \dots \quad (1-8)$$

Since nucleons have spin $\frac{1}{2}$, they are *fermions* and hence must be associated with wavefunctions that are *totally antisymmetric*. This means that in building up many-nucleon states the Pauli exclusion principle must be followed. Many-nucleon states may be constructed by filling the spin-orbitals with neutrons and protons up to their maximum allowed occupancy. The building-up principle is very similar to that for

periodic table for atoms except one fills neutron and proton orbitals separately to construct nuclei with given A , N , Z numbers.

1.3 MAGIC NUCLEI NUMBERS

Nuclei in which the proton and neutron numbers Z, N belong to the *magic numbers*

$$\text{Nuclei Magic Numbers } 2, 8, 20, 28, 50, 82, 126 \quad (1-9)$$

tend to be exceptionally stable and evidently associated with the closure of shells. The magic numbers 2, 8, 20 correspond to the closure of the shells corresponding to the first, second and third levels of an isotropic 3-dimensional harmonic oscillator. But closure of the fourth level would give the fourth magic number as 40 rather than 28. This constituted a puzzle until Goeppert Mayer introduced the spin-orbit interaction into the nuclear shell model. In her case the spin-orbit interaction has the *opposite sign* to the conventional spin-orbit interaction of electrons. This means, for example, that in the $1p$ shell the $1p_{3/2}$ level is *below* the $1p_{1/2}$ level whereas in atoms one has the opposite ordering. The effect of introducing the spin-orbit interaction is also to partially lift the single particle energy degeneracies so that, apart from the case of s -states each orbital ℓ becomes characterized by a total single particle angular momentum

$$j_{\pm} = \ell \pm s \quad (1-10)$$

Henceforth, let us use n as the *nodal* quantum number rather than as the harmonic oscillator level number so that a given spin-orbital is designated by the single particle quantum numbers $n\ell jm$. For a single nucleon moving in a nucleus we write the spin-orbit interaction as

$$V_{s.o} = \zeta(r)_{n\ell} (\mathbf{s} \cdot \boldsymbol{\ell}) \quad (1-11)$$

where $\zeta(r)_{n\ell}$ is the *spin-orbit coupling constant* which is a *radial* function dependent on the nature of the nuclear field and upon the quantum numbers $n\ell$. For a single nucleon

$$(\mathbf{s} \cdot \boldsymbol{\ell}) = \frac{1}{2} [j(j+1) - \ell(\ell+1) - \frac{3}{4}] \quad (1-12)$$

The energy separation between the two components of a spin-orbit split doublet characterized by the quantum numbers $n\ell$ becomes

$$\Delta E_{n\ell} = \left(\ell + \frac{1}{2}\right) \zeta(r)_{n\ell} \quad (1-13)$$

Thus the level with j_+ is *lower* than the level with j_- . Furthermore, it is a practical observation that states with higher values of ℓ have larger doublet splittings.

Even with the introduction of the spin-orbit interaction the single nucleon degeneracy is only partially lifted. The degeneracy associated with the isotropic harmonic

oscillators is partially lifted so that states of a given harmonic oscillator level are no longer degenerate with respect to ℓ while each set of states associated with a particular orbital angular momentum ℓ is split as a doublet of degenerate states labeled by the quantum numbers $n\ell jm$. The degeneracy with respect to the *total angular momentum projection quantum number* m remains, and hence each level with total angular momentum j is $(2j + 1)$ -fold degenerate. The spin-orbit splitting leads to subshells with a given j -level accommodating up to $2j + 1$ protons or neutrons.

1.4 NUCLEAR PAIRING INTERACTIONS

It is remarkable that nuclei having *even* numbers of protons *and* neutrons, so called *even-even* nuclei, are always found to have zero nuclear angular momentum, i.e. $I = 0$. In nuclear physics the total angular momentum $J = L + S$ is nevertheless usually referred to as the *nuclear spin* and designated by the letter I . So called *odd-even* and *even-odd* nuclei always have *half-integer* nuclear spin while *odd-odd* nuclei always have *integer* nuclear spin. It would appear that *even* numbers of neutrons or protons *pair* to produce a lowest energy state, which has nuclear spin $I = 0$. Indeed, Racah, showed that a strong short range nuclear force, such as a delta type force, leads to such a pairing. It is this feature that is the key to predicting the nuclear spin of the ground states of nuclei. If there is an even number of protons or neutrons in a given orbital then those orbitals make no contribution to the nuclear spin of the ground state. Furthermore, there is no nuclear spin contribution from closed shells.

1.4.1 SENIORITY AND PAIRING INTERACTIONS

Racah introduced the concept of *seniority* in both atomic and nuclear physics (and indeed also in superconductivity where pairing is also important). He showed that for a strong pairing interaction such as occur in nuclei states of lowest seniority number v lie lowest. Thus in a configuration of identical nucleons, j^N , the integer, $[\frac{N-v}{2}]$, corresponds to the number of pairs of particles that are coupled to zero angular momentum where

$$v = \begin{cases} 0, 2, \dots, N & N \text{ even} \\ 1, 3, \dots, N & N \text{ odd} \end{cases} \quad (1-14)$$

This has the consequence that in a configuration j^N if N is *even* then the lowest state will have zero angular momentum, whereas if N is *odd* the angular momentum of the lowest state will be $J = j$.

In the case of atoms however, where there is Coulomb repulsion between pairs of electrons, states of maximal seniority lie lowest and hence in some respects nuclear states are simpler than electronic states!

The angular momentum states J and seniority numbers for the identical particle configurations j^N are given for $j = \frac{1}{2}, \frac{3}{2}, \dots, \frac{7}{2}$ in Table 1-1. For $j = \frac{5}{2}, \frac{7}{2}$ we list just the states up to $N = j + \frac{1}{2}$.

TABLE 1-1
Angular Momentum J and Seniority Numbers
for Some j^N Configurations

j^N	J	v	$\frac{N-v}{2}$
$(\frac{1}{2})^0$	0	0	0
$(\frac{1}{2})^1$	$\frac{1}{2}$	1	0
$(\frac{1}{2})^2$	0	0	1
$(\frac{3}{2})^0$	0	0	0
$(\frac{3}{2})^1$	$\frac{3}{2}$	1	0
$(\frac{3}{2})^2$	0	0	1
	2	2	0
$(\frac{3}{2})^3$	$\frac{3}{2}$	1	1
$(\frac{3}{2})^4$	0	0	2
$(\frac{5}{2})^0$	0	0	0
$(\frac{5}{2})^1$	$\frac{5}{2}$	1	0
$(\frac{5}{2})^2$	0	0	1
	2, 4	2	0
$(\frac{5}{2})^3$	$\frac{5}{2}$	1	1
	$\frac{3}{2}, \frac{9}{2}$	3	0
$(\frac{7}{2})^0$	0	0	0
$(\frac{7}{2})^1$	$\frac{7}{2}$	1	0
$(\frac{7}{2})^2$	0	0	1
	2, 4, 6	2	0
$(\frac{7}{2})^3$	$\frac{7}{2}$	1	1
	$\frac{3}{2}, \frac{5}{2}, \frac{9}{2}, \frac{11}{2}, \frac{15}{2}$	3	0
$(\frac{7}{2})^4$	0	0	2
	2, 4, 6	2	1
	2, 4, 5, 8	4	0

1.5 NUCLEAR SPIN OF NUCLEI GROUND STATES

In atomic physics interest is almost entirely restricted to atomic effects involving nuclei in their ground states. A given isotope is characterized by the number of neutrons, N , and number of protons, Z . Starting with Table 1-1 giving the ordering of the $n\ell j$ quantum numbers for a single nucleon in an isotropic three-dimensional harmonic oscillator potential together with the spin-orbit interaction, we can determine the nuclear spin of the ground states of most nuclei. Let us now consider some examples.

1.5.1 NUCLEAR SPIN OF H AND He ISOTOPES

Hydrogen has three well-known isotopes, hydrogen, 1_1H , deuterium, 2_1H , and tritium, 3_1H . Hydrogen involves a single proton that may be assigned to the $(1s_{1/2})^1_p$ configuration and hence 1_1H has a nuclear spin $I = \frac{1}{2}$. Deuterium has a single proton and neutron, and hence the nuclear ground state configuration is $(1s_{1/2})^1_p(1s_{1/2})^1_n$. The nuclear spin results from the coupling of two $\frac{1}{2}$ spins to produce $I = 0, 1$. Experiment shows that the ground state has $I = 1$. Finally, tritium has a single proton and two neutrons, and therefore the nuclear configuration is $(1s_{1/2})^1_p(1s_{1/2})^2_n$. The two neutrons close the $1s_{1/2}$ shell and hence make no contribution to the nuclear spin, and thus the nuclear spin of the tritium nucleus is $I = \frac{1}{2}$, the same as for hydrogen. Note that in each case the ground state has *even* parity.

The two principal isotopes of helium are 4_2He and 3_2He . For the more abundant isotope, 4_2He , we have the nuclear configuration $(1s_{1/2})^2_p(1s_{1/2})^2_n$, and both shells are closed. Hence the nuclear spin is $I = 0$, whereas for 3_2He we have the nuclear configuration $(1s_{1/2})^2_p(1s_{1/2})^1_n$ and a nuclear spin of $I = \frac{1}{2}$.

1.5.2 SILICON ISOTOPES

Silicon has three stable isotopes, ${}^{28}_{14}Si$ (92.23%), ${}^{29}_{14}Si$ (4.67%), ${}^{30}_{14}Si$ (3.10%). Two of the isotopes are *even-even* nuclei, and both have nuclear spin and parity $I = 0^+$. All three isotopes have $Z = 14$, and therefore the 14 protons occur in the proton configuration $(1s^2_{1/2} 1p^4_{3/2} 1p^2_{1/2} 1d^6_{5/2})$. In practice we normally omit all closed shells except for the highest and thus write the configuration as simply $(1d^6_{5/2})_p$. Since the proton number is *even*, it follows that the protons make no contribution to the nuclear spin. Fourteen of the neutrons go into the same type of configuration as the protons with the fifteenth neutron occupying the $(2s_{1/2})_n$ orbital. Thus the nuclear spin of ${}^{29}_{14}Si$ is $I = \frac{1}{2}^+$.

The above observations are of significance in considering the possibility of using silicon in quantum computing. Only the ${}^{29}_{14}Si$ nuclei will respond to an external magnetic field. Isotopically pure ${}^{28}_{14}Si$ with nuclear spin $I^p = 0^+$ gives no response to magnetic fields. Phosphorus has one stable isotope ${}^{31}_{15}P$ with one unpaired proton in the $2s_{1/2}$ shell, and hence nuclear spin $I^p = \frac{1}{2}^+$. Noting these facts, Kane² has proposed building a quantum computer using ${}^{28}_{14}Si$ doped with ${}^{31}_{15}P$.

1.5.3 RUBIDIUM ISOTOPES

Rubidium has two stable isotopes, ${}^{85}_{37}Rb$ (72.16%), ${}^{87}_{37}Rb$ (27.83%) (actually the isotope ${}^{87}_{37}Rb$ is slightly unstable with a half-life of $t_{1/2} = 4.75 \times 10^{10}$ y). The two nuclei are *odd-even* with the neutrons making no contribution to the nuclear spin. The first 28 protons go into filling closed shells leaving a further nine protons to be distributed among the $2p_{3/2}$ and $1f_{5/2}$ orbitals. Eight of the protons will pair to produce no contribution to the nuclear spin leaving one unpaired proton. Experimentally it is found that for ${}^{85}_{37}Rb$ the nuclear spin is $I^p = \frac{5}{2}^-$ while for ${}^{87}_{37}Rb$

$I^p = \frac{3}{2}^-$. These results show some of the limitations of the simple nuclear shell model, but as always, final appeal must be made to experiment. For an excellent data base on properties of isotopes go to <http://ie.lbl.gov/education/isotopes.htm> or to <http://www.webelements.com/webelements/elements/text/periodic-table/isot.html>; the latter gives the Periodic Table and nuclear magnetic moments.

The rubidium isotopes play a key role in studies of *Bose-Einstein Condensation (BEC)*. Rubidium atoms behave as *bosons*, since their nuclear spins are half-integer. However, the number of their electrons is *odd*, and therefore the net electron angular momentum J is necessarily half-integer. The total angular momentum of the atom F comprises the vector addition of the nuclear spin I and electronic angular momentum J such that

$$\mathbf{F} = \mathbf{J} + \mathbf{I} \quad (1-15)$$

F is thus necessarily an integer and the rubidium atoms behave as *bosons*.

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2 Notes on the Quantum Theory of Angular Momentum

Pure mathematics is on the whole distinctly more useful than applied. For what is useful above all is technique, and mathematical technique is taught mainly through pure mathematics

G H Hardy

In the language, and within the understanding, of the quantum mechanics the symmetry of a many particle system is determined by the transformation properties of the Hamiltonian. Among the collection of all transformations those that commute with the Hamiltonian are *symmetry operations*. The commutation relations mean that the Hamiltonian remains invariant under the action of the symmetry operations. Keeping in mind our future applications of the tools of quantum mechanics for evaluation of various matrix elements, in the case of free atoms and ions, the most important are the symmetry operations of the rotation group in three dimensions, $SO(3)$. The angular momentum operators are the generators of all the rotations in three dimensional space. As a consequence, the Hamiltonian of spherically symmetric systems have to commute with the generators of the symmetry operators. In this particular case it means that Hamiltonian has to commute with the angular momentum operators. Consequently, the basic property of the hermitan operators states that if two operators commute, they have a common set of the eigenfunctions (but not the same eigenfunctions!) and simultaneously measured eigenvalues. As a result the energy states carry also information about the eigenvalues of angular momentum operators (only of these that commute with the Hamiltonian). These transformation properties, distinguished by the eigenvalues of appropriate angular momentum operators, are the formal source of the quantum numbers that identify the energy states of a many electron system. At the same time, the spherical harmonics form the basis sets for the irreducible representations of the three dimensional rotation group. In the case of the systems of symmetry lower than spherical, as in the case of crystals, the transformation properties are defined by the point groups, and the identification of the energy states is also based on the commutation relations of the Hamiltonian and the symmetry operators. In such cases, instead of quantum numbers, the irreducible representations of a given group directly identify the energy levels.

We review some basic aspects of the quantum theory of angular momentum, which is needed in the further discussion. In making practical calculations we must ultimately be able to evaluate the matrix elements of interactions in suitable angular momenta bases.

2.1 COUPLING AND UNCOUPLING OF ANGULAR MOMENTA

Consider the components, J_x , J_y and J_z of the angular momentum vector \mathbf{J} that satisfy the commutation relations (we shall normally put $\hbar = 1$),

$$[J_x, J_y] = iJ_z, \quad [J_y, J_z] = iJ_x, \quad [J_z, J_x] = iJ_y \quad (2-1)$$

States that are simultaneous eigenfunctions of \mathbf{J}^2 and J_z are designated in Dirac's ket notation as $|JM\rangle$. Thus the standard angular momentum operator relations have the form

$$\mathbf{J}^2|JM\rangle = J(J+1)|JM\rangle \quad (2-2a)$$

$$J_z|JM\rangle = M|JM\rangle \quad (2-2b)$$

$$J_{\pm}|JM\rangle = [J(J+1) - M(M \pm 1)]^{\frac{1}{2}}|JM \pm 1\rangle \quad (2-2c)$$

where

$$J_{\pm} = J_x \pm iJ_y \quad (2-3)$$

are the usual angular momentum ladder operators.

For a given eigenvalue J there are $2J + 1$ values of the M quantum number

$$M = -J, J - 1, \dots, J - 1, J \quad (2-4)$$

and for the states with the maximum and minimum values of M

$$J_+|JJ\rangle = 0 \quad J_-|J-J\rangle = 0 \quad (2-5)$$

It is a common problem in the quantum theory of angular momentum to couple together two ket states, say $|j_1m_1\rangle$, $|j_2m_2\rangle$ to produce coupled states $|(j_1j_2)jm\rangle$. Thus to have

$$|j_1m_1\rangle|j_2m_2\rangle = \sum_{j,m} \langle jm|m_1m_2\rangle |(j_1j_2)jm\rangle \quad (2-6)$$

or inversely to uncouple coupled states, the *coupling coefficients* or *Clebsch-Gordan coefficients* $\langle j_1m_1j_2m_2|j_1j_2jm\rangle$ are introduced. They represent the elements of a unitary transformation that couples the uncoupled states $|j_1m_1\rangle|j_2m_2\rangle$ to produce the coupled states $|(j_1j_2)jm\rangle$,

$$|(j_1j_2)jm\rangle = \sum_{m_1,m_2} \langle j_1m_1j_2m_2|j_1j_2jm\rangle |j_1m_1\rangle|j_2m_2\rangle \quad (2-7)$$

Such transformations arise, for example in relating basis states in the $|SM_SLM_L\rangle$ scheme to the coupled basis states $|SLJM\rangle$, where $M = M_S + M_L$. Thus,

$$|SLJM\rangle = \sum_{M_S,M_L} \langle M_S M_L | SLJM \rangle |SM_SLM_L\rangle \quad (2-8)$$

Note that we shall often abbreviate the Clebsch-Gordan coefficient $\langle j_1m_1j_2m_2|j_1j_2jm\rangle$ to just $\langle m_1m_2|j_1j_2jm\rangle$.

As an example we analyze the triply ionized thulium Tm^{3+} , which has as its ground state the spectroscopic term $4f^{12} {}^3H_6$. This means that the state is described by the quantum numbers $S = 1$, $L = 5$, and $J = 6$. The state is $(2J + 1) = 13$ -fold degenerate, and the degenerate states are distinguished by the quantum number M . These states could be described by the kets $|SLJM\rangle$ in the so-called *Russell-Saunders* or LS -coupling, where S is coupled to L to give a total angular momentum J . Alternatively the states could be described by the kets defined in an uncoupled momenta scheme, $|SM_SLM_L\rangle$. These two sets of states correspond to two different bases that are linked by the Clebsch-Gordan coupling coefficients as in (2-8). For maximal M we expect for the ground state that

$$|(1, 5)66\rangle \equiv e^{i\phi}|(1, 1)(5, 5)6\rangle \quad (2-9)$$

where the left-hand ket is in the $(SL)JM$ scheme, and the right-hand in the $(SM_S)(LM_L)$ scheme, and $e^{i\phi}$ is a phase factor, which we choose as unity. In fact, at this point the choice of the phase factor is arbitrary, since the wave functions, by themselves, do not have any physical interpretation, and only their squared modulus, that cancels all signs, does. However, any phase factor convention once chosen has to be followed throughout the course of the calculations.

The other states in the $SLJM$ scheme that are assigned to the remaining values of the quantum numbers are expressed as linear combinations of those in the SM_SLM_L scheme. As an example we determine some of these linear combinations. First note that

$$J_{\pm} = L_{\pm} + S_{\pm} \quad (2-10)$$

Let us apply the lowering ladder operator to both sides of (2-9), using at the left-hand-side its form from the left hand-side of (2-10), and consequently, using its form from the right-hand-side of (2-10) to the right-hand-side of (2-9), namely

$$J_-|(1, 5)66\rangle = \sqrt{6(6+1) - 6(6-1)}|(1, 5)65\rangle = \sqrt{12}|(1, 5)65\rangle \quad (2-11a)$$

$$\begin{aligned} L_- + S_-|(1, 1)(5, 5)6\rangle &= \sqrt{5(5+1) - 5(5-1)}|(1, 1)(5, 4)5\rangle \\ &\quad + \sqrt{1(1+1) - 1(1-1)}|(1, 0)(5, 5)5\rangle \\ &= \sqrt{10}|(1, 1)(5, 4)5\rangle + \sqrt{2}|(1, 0)(5, 5)5\rangle \end{aligned} \quad (2-11b)$$

Equating (2-11a) and (2-11b) gives

$$|(1, 5)65\rangle = \frac{1}{\sqrt{6}} \left[\sqrt{5}|(1, 1)(5, 4)5\rangle + |(1, 0)(5, 5)5\rangle \right] \quad (2-12)$$

Using the ladder operators in the way presented in the example above it is possible to find the coefficients of all the other linear combinations that define the states of the $4f^{12}$ configuration of thulium ion. In order to make this procedure more straightforward, the subsequent application of (2-2c) to lower the values of the quantum numbers to desired values (in some cases the operators have to be applied several times), the Clebsch-Gordan coefficients are introduced. The concept of these coefficients as transformation matrices between coupled and uncoupled angular momenta

schemes is presented in (2-6) and (2-7); their algebraic form is as follows

$$\begin{aligned} \langle m_1 m_2 | j_1 j_2 j m \rangle = & \\ \delta_{m_1+m_2, m} \sqrt{\frac{(2j+1)(j_1+j_2-j)! (j_1-m_1)! (j_2-m_2)! (j+m)! (j-m)!}{(j_1+j_2+j+1)! (j+j_1-j_2)! (j-j_1+j_2)! (j_1+m_1)! (j_2+m_2)!}} & \\ \times \sum_z (-1)^{j_1-m_1-z} \frac{(j_1+m_1+z)! (j+j_2-m_1-z)!}{z! (j-m-z)! (j_1-m_1-z)! (j_2-j+m_1+z)!} & \quad (2-13) \end{aligned}$$

where the summation is performed over such values of z for which all the factorials are well defined (the arguments are positive).

2.2 THE $3j$ -SYMBOLS

While Clebsch-Gordan coefficients possesses considerable symmetry and from their structure it is possible to verify the coupling scheme of angular momenta, a more symmetrical object was defined by Wigner and is now commonly known as the $3j$ -symbol or $3jm$ -symbol. The $3j$ -symbol is related to the Clebsch-Gordan coefficient by

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1-j_2-m_3} \frac{\langle m_1 m_2 | j_1 j_2 j_3 - m_3 \rangle}{\sqrt{(2j_3+1)}} \quad (2-14)$$

The $3j$ -symbol is invariant with respect to an *even* permutation of its columns, while for *odd* permutations of its columns is multiplied by a phase factor equal to the sum of the arguments in its top row,

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} \quad (2-15)$$

Furthermore, changing the sign of all three lower arguments results also in multiplication by a phase factor equal to the sum of the arguments in its top row,

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} \quad (2-16)$$

A $3j$ -symbol having all its m quantum numbers zero vanishes unless $j_1 + j_2 + j_3$ is *even*. Likewise any $3j$ -symbol having two identical columns will vanish unless $j_1 + j_2 + j_3$ is *even*.

The unitarity property of the Clebsch-Gordan coefficients leads directly to the orthonormality conditions for the $3j$ -symbols

$$\sum_{j_3, m_3} (2j_3+1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m'_1 & m'_2 & m_3 \end{pmatrix} = \delta_{m_1, m'_1} \delta_{m_2, m'_2} \quad (2-17a)$$

$$\sum_{m_1, m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j'_3 \\ m_1 & m_2 & m'_3 \end{pmatrix} = \frac{\delta_{j_3, j'_3} \delta_{m_3, m'_3}}{2j_3+1} \quad (2-17b)$$

The values of the angular coupling coefficients are collected in various tables.

2.3 THE $6j$ -SYMBOLS

The $6j$ -symbol is defined by the relation

$$\begin{aligned} & ((j_1 j_2) j_{12}, j_3; j m | j_1, (j_2 j_3) j_{23}; j m) \\ &= (-1)^{j_1+j_2+j_3+j} \sqrt{(2j_{12}+1)(2j_{23}+1)} \left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{matrix} \right\} \end{aligned} \quad (2-18)$$

Similarly as in the case of the $3j$ -symbols also here it is possible to analyze the coupling schemes of angular momenta on both sides of the transformation matrix. Indeed, it is seen that in general the $6j$ -symbols connect two schemes of coupling of three momenta. The $6j$ -symbol may be evaluated by first expressing it as a sum over a triple product of $3j$ -symbols and then using the fact that the $6j$ -symbol is independent of m to produce a sum involving a single variable to finally yield

$$\begin{aligned} \left\{ \begin{matrix} a & b & c \\ d & e & f \end{matrix} \right\} &= \sqrt{\Delta(abc)\Delta(aef)\Delta(dbf)\Delta(dec)} \times \sum_z (-1)^z (z+1)! \\ &\times [(z-a-b-c)!(z-a-e-f)!(z-d-b-f)! \\ &\times (z-d-e-c)!(a+b+d+e-z)!(b+c+e+f-z)! \\ &\times (a+c+d+f-z)!]^{-1} \end{aligned} \quad (2-19)$$

where

$$\Delta(abc) = [(a+b-c)!(a-b+c)!(b+c-a)/(a+b+c+1)!]^{\frac{1}{2}}$$

which also represents the triangular condition that has to be satisfied for its arguments. In particular, the $6j$ -symbol vanishes unless the four triangular conditions portrayed below are satisfied (all four are represented by appropriate Δ 's under the square root in the above expression),

$$\begin{aligned} & \left\{ \begin{matrix} & & \circ & & \\ & \ddots & & \ddots & \\ \circ & & & & \circ \end{matrix} \right\} \left\{ \begin{matrix} \circ & \dots & \circ & \dots & \circ \\ & & & & \\ & & & & \end{matrix} \right\} \\ & \left\{ \begin{matrix} & & & & \circ \\ & & & \ddots & \\ \circ & \dots & \circ & & \end{matrix} \right\} \left\{ \begin{matrix} \circ & & & & \\ & \ddots & & & \\ & & \circ & \dots & \circ \end{matrix} \right\} \end{aligned} \quad (2-20)$$

where for example $|a-b| \leq c \leq a+b$.

The $6j$ -symbol is invariant with respect to any interchange of columns and also with respect to the interchange of the upper and lower arguments of any two columns. The $6j$ -symbols satisfy the orthogonality condition

$$\sum_{j_{12}} (2j_{12}+1)(2j_{23}+1) \left\{ \begin{matrix} j_3 & j & j_{12} \\ j_1 & j_2 & j_{23} \end{matrix} \right\} \left\{ \begin{matrix} j_3 & j & j_{12} \\ j_1 & j_2 & j'_{23} \end{matrix} \right\} = \delta_{j_{23}, j'_{23}} \quad (2-21)$$

2.4 THE $9j$ -SYMBOL

The $6j$ -symbol arose in discussing the coupling of three angular momenta. Clearly more complex nj -symbols arise for couplings that involve more than three angular momenta. The $9j$ -symbol is defined as a transformation matrix between two coupling schemes of four angular momenta

$$\begin{aligned} & ((j_1 j_2) j_{12}, (j_3 j_4) j_{34}; j | (j_1 j_3) j_{13}, (j_2 j_4) j_{24}; j) \\ &= \sqrt{(2j_{12} + 1)(2j_{34} + 1)(2j_{13} + 1)(2j_{24} + 1)} \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{Bmatrix} \quad (2-22) \end{aligned}$$

The $9j$ -symbol may be expressed in terms of $6j$ -symbols as

$$\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{Bmatrix} = \sum_z (-1)^{2z} [z] \begin{Bmatrix} a & d & g \\ h & i & z \end{Bmatrix} \begin{Bmatrix} b & e & h \\ d & z & f \end{Bmatrix} \begin{Bmatrix} c & f & i \\ z & a & b \end{Bmatrix} \quad (2-23)$$

The $9j$ -symbol is left invariant with respect to any *even* permutation of its rows or columns or a transposition of rows and columns. Under an *odd* permutation of rows or columns the symbol is invariant but for a phase factor equal to the sum of its all arguments. If one argument of the $9j$ -symbol is zero the symbol collapses to a single $6j$ -symbol, namely

$$\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & 0 \end{Bmatrix} = \delta_{c,f} \delta_{g,h} \frac{(-1)^{b+d+f+g}}{\sqrt{(2c+1)(2g+1)}} \begin{Bmatrix} a & b & c \\ e & d & g \end{Bmatrix} \quad (2-24)$$

2.5 TENSOR OPERATORS

A fundamental problem of quantum mechanical description of many particle systems is to calculate matrix elements of relevant interactions. To do this in an elegant and efficient way one has to express the interactions in terms of tensor operators as pioneered by Racah¹⁻⁴ and outlined by Judd⁵ and Edmonds⁶. The theory of tensor operators has a deep group theoretical basis, which is not considered here⁵⁻⁸. Here we follow Racah's original introduction of tensor operators². An *irreducible tensor operator* $\mathbf{T}(k)$, of rank k has $(2k + 1)$ components $T(kq)$ where $q = -k, -k + 1, \dots, k - 1, k$, which satisfy the commutation relations

$$[J_z, T(kq)] = qT(kq) \quad (2-25a)$$

$$[J_{\pm}, T(kq)] = \sqrt{k(k+1) - q(q \pm 1)} T(k, q \pm 1) \quad (2-25b)$$

Group theoretically this implies that the tensor operator components form a basis for the $(2k + 1)$ -dimensional irreducible representation $[k]$ of the rotation group in three dimensions, $SO(3)$. Furthermore since the components satisfy the same commutation relations, they can be regarded as objects that transform themselves like angular momentum states $|kq\rangle$. As a result we can use standard angular momentum

coupling techniques to form coupled products of tensor operators. For a rank $k = 1$ tensor operator we have, in terms of the Cartesian components (T_x, T_y, T_z)

$$T_{\pm 1}^{(1)} = \frac{\mp 1}{\sqrt{2}}(T_x \pm iT_y), \quad T_0^{(1)} = T_z \quad (2-26)$$

Thus \mathbf{J} is a tensor operator of rank $k = 1$ with components

$$J_0^{(1)} = J_z, \quad J_{\mp 1}^{(1)} = \pm \frac{J_{\mp}}{\sqrt{2}} \quad (2-27)$$

A more complex example is the Coulomb interaction and its tensorial form. The matrix elements of the N -particle repulsive Coulomb interaction

$$H_c = \sum_{i < j}^N \frac{e^2}{r_{ij}} \quad (2-28)$$

play an important role in atomic physics. The interaction between each pair of electrons may be expanded in terms of Legendre polynomials of the cosine of the angle ω_{ij} between the vectors from the nucleus to the two electrons as

$$\frac{e^2}{r_{ij}} = e^2 \sum_k \frac{r_{<}^k}{r_{>}^{k+1}} P_k(\cos \omega_{ij}) \quad (2-29)$$

where $r_{<}$ indicates the distance from the nucleus of the nearer electron and $r_{>}$ the distance from the nucleus to the further away electron. Using the spherical harmonic addition theorem⁹ it is possible to obtain the angular part of the Coulomb interaction operator in a tensorial form

$$\begin{aligned} P_k(\cos \omega_{ij}) &= \frac{4\pi}{2k+1} \sum_q Y_{kq}^*(\theta_i, \phi_i) Y_{kq}(\theta_j, \phi_j) \\ &= \sum_q (-1)^q (C_{-q}^{(k)})_i (C_q^{(k)})_j \\ &= (\mathbf{C}_i^{(k)} \cdot \mathbf{C}_j^{(k)}) \end{aligned} \quad (2-30)$$

where the *spherical tensors* $C_q^{(k)}$ are defined in terms of the usual spherical harmonics, Y_{kq} (that obviously satisfy (2-25a) and (2-25b), and therefore formally are also tensor operators) as

$$C_q^{(k)} = \left(\frac{4\pi}{2k+1} \right)^{1/2} Y_{kq} \quad (2-31)$$

The $C_q^{(k)}$ are the components of tensor operator $\mathbf{C}^{(k)}$ with a rank k , and $(\mathbf{C}_i^{(k)} \cdot \mathbf{C}_j^{(k)})$ denotes the *scalar product* of two spherical tensors.

2.6 THE WIGNER-ECKART THEOREM FOR $SO(3)$

The key for calculating the matrix elements of tensor operators that act between angular momentum states comes from the Wigner-Eckart theorem as applied to $SO(3)$.