Symmetry and Spectroscopic Calculations

Lecture One

1.1 Introduction

In this course of lectures I want to introduce you to the role of symmetry in making practical calculations of spectroscopic properties of atoms. However, many of the techniques we shall consider have an applicability in other areas of physics such as can be encountered in nuclear physics, particle physics, molecular physics and solid-state physics. This is because the concepts of symmetry are universal in there applicability in physics. Indeed they are profoundly unifying concepts. Throughout we will emphasise practical methods rather than abstract theory. Thus we shall try to explain results but will not be going into formal proofs. I will be expecting you to apply these results in calculations for models of real systems. Note I say *models* of real systems. Every calculation is associated with a particular model that will never correspond exactly to a real system in its full diversity. Nevertheless we would hope that some of our calculations will be a good approximation to some system.

To start we will first consider just what we mean by symmetry and then review some of the properties of symmetric functions which arise in the theory of the symmetric group. There we will encounter some of the basic ideas of mathematical groups which is that area of mathematics that allows us to create a framework to develop applications of symmetry. Among the various symmetric functions considered will be the so-called Schur functions. These functions play a key role in calculation of the properties of not only the symmetric group but perhaps more importantly for us properties of the continuos Lie groups such as the unitary and rotation groups. The key results here will be the Littlewood-Richardson rule for multiplying Schur functions, the use of Young tableaux, Young's remarkable description of the representations of the symmetric group S_n and the Murnaghan-Nakayama procedure for calculating characters of S_n.

I shall be assuming you have some knowledge of the quantum theory of angular momentum such as commonly associated with the angular momentum states $|JM>$ and the use of ladder operators. I shall use that knowledge to develop the theory of tensor operators which allow us to go beyond just symmetry to develop quantitative calculations via the celebrated Wigner-Eckart theorem. Here we will encounter the $3j-$ and $6j-$ symbols of angular momentum which will allow us to calculate matrix elements of interactions, first for simple one- and two-electron systems and, with further development, for $n-$electron systems.

In some cases the calculations we shall attempt will be very simple, the sort of back-of-the-envelope calculations so dear to many physicists. Other calculations will require extensive computation best left to computer algebraic packages such as Maple or Mathematica. As to group theory calculations I shall take the opportunity to introduce you to the package

SCHUR that takes the tedium out of many practical applications. I think it is very important to have practice at making simple hand calculations first before jumping into heavy computer based calculations. We need also to develop procedures for checking calculations.

Among the calculations I would like us to investigate will be such things as magnetic interactions, hyperfine structure, transition probabilities, and crystal field interactions. I would also like to emphasise ideas of effective interactions and *ab initio* calculations.

1.2 Why Symmetry?

Symmetry is usually associated with an action or transformation of a system or object such that after carrying the operation the system or object is in a state indistinguishable from that which it had prior to carrying out the action or transformation. Thus there is a close relationship between symmetry and impossible experiments. The existence of a symmetry implies that it is impossible to devise an experiment to distinguish the before and after situation. If you succeed then the symmetry does not exist. All the great conservation laws are associated with the assertion that a particular experiment is impossible. Indeed in the early 1900's Emmy Nöether showed that every conservation law is associated with a certain invariance which in turn is associated with the statement of an impossible experiment. For example, the conservation of angular momentum is associated with the statement that no experimentalist has been able to determine a preferred direction in space.

Thus the existence of a symmetry tells us what is NOT possible but does not tell us what IS possible. Thus the symmetry rules out some possibilities. It leads to *selection rules*. The existence of a symmetry constrains the form of theories used to model the system possessing an observed symmetry. We must strongly emphasise that the existence of a symmetry can only be determined by experiment and is always a tentative statement. We can never be sure that some improvement in experimental technique or some experiment not hitherto contemplated will reveal an inexactitude in the symmetry. As examples consider the parity violation experiment or the CP violation experiments of kaons. In practice very few symmetries are 'exact' and in most cases we are led to consider 'approximate' symmetries. A symmetry need not be exact to be useful. Indeed I would assert the following:

Proposition: *We should always strive to construct theories with the highest possible symmetry even if these are not exact symmetries of nature. The physics comes in the process of breaking the symmetry.*

1.3 An example

Consider the case of

$$Ce_2Mg_3(NO_3)_{12} \cdot 24H_2O : Nd^{3+}$$

What symmetry does the Nd^{3+} ion see in the rare earth double nitrates? In free space it sees spherical symmetry associated with the three-dimensional rotation group SO_3. The total electron angular momentum J has no preferred direction in free space and is a conserved quantity.* Associated with the conservation of the angular momentum J is a *degeneracy* of $(2J + 1)$ since each component J_z occurs at the same energy. Switch on a magnetic field in the $z-$direction and create a locally preferred direction and the degeneracy is *lifted* and we observe $2J + 1$ sublevels.**

Placing the Nd^{3+} ion in the crystal breaks the spherical symmetry so that J ceases to be a conserved quantity - there are local preferred directions imposed by the geometrical arrangement of the various ions clustering about the Nd^{3+} ion. To a first approximation we descend to the symmetry group of the icosahedron K_h and for $J \geq \frac{5}{2}$ there will be a partial lifting of the $(2J + 1)-$fold degeneracy.

The nitrate ions cluster around the vertices of a slightly distorted tetrahedron and the symmetry is approximately that of the group of the tetrahedron, T_h. Again the degeneracy is further reduced. These reductions in degeneracy manifest themselves in the appearance of sublevels. The actual point symmetry observed by $X-$ray structural analysis is that of the trigonal point group, C_3.

Thus the entire breakdown of the symmetry could be described by the chain of nested subgroups ***

$$SO_3 \supset K_h \supset T_h \supset C_3$$

1.4 Global and Local Symmetries

A symmetry may be *global* or *local*. As already seen in the previous example a local symmetry need not be global. In most of this course we will discussing local symmetries.

1.5 Types of Symmetries

There are a wide range pf possible symmetries we might consider. Two major categories would be *discrete* and *continuous* symmetries. Discrete symmetries, such as reflections, inversions, time reversal, charge conjugation, parity, finite rotations, permutations etc. are associated with *multiplicative* or *phase-like* quantum numbers. Continuous symmetries such as translations and rotations are associated with *additive* quantum numbers (e.g. angular momentum $\mathbf{J}$ or linear momentum $\mathbf{p}$).

*Of course if we recognise that Nd^{3+} possesses a nuclear magnetic moment which weakly couples the nuclear angular momentum I to the electronic angular momentum J such that the total angular momentum becomes $\mathbf{F} = \mathbf{I} + \mathbf{J}$. Thus strictly speaking the conserved quantity is F rather than J. This is manifested in the appearance of magnetic hyperfine structure at high enough resolution.

**N.B. Lowering the symmetry of a system usually results in a partial or total lifting of the degeneracy. Technologically this is *very* important.

***For further details see S.D.Devine, T_h *symmetry in rare earth double nitrates* J.Chem.Phys. **47**, 1844 (1967) and references therein.

1.6 Bosons and Fermions

The particles we commonly encounter in physics can be divided into two classes *bosons* and *fermions*. Bosons are associated with *integer* spin, examples being photons, gluons and the weak interaction bosons Z^0 and $W^{\pm}$. Fermions are associated with *half-integer* spin, examples being electrons, neutrinos and quarks. Bosons establish the *interactions* between fermions. Thus the *photon*, a massless spin 1 particle, is the exchange particle associated with electromagnetic interactions. In most of atomic and molecular physics we can restrict our attention to quantum electrodynamics (QED). The weak interactions manifest themselves in atomic and molecular physics in very small parity violations. Bosons and fermions obey different statistics, namely Bose-Einstein and Fermi-Dirac, respectively. That requires us to construct totally symmetric wavefunctions for many-boson systems and totally antisymmetric wavefunctions for many-fermion systems.

1.7 Permutational Symmetry

Bosons and fermions differ with respect to their behaviour under an interchange of their position, or equivalently with respect to a rotation through 2π or 360^o. We shall designate the wavefunction for a single fermion or boson as $\phi(\alpha)$ where α is an appropriate set of single particle quantum numbers associated with some single particle solution of , for example, some central field potential. Thus for a hydrogen atom we might use $\alpha = \{ns\ell m_s m_\ell\}$ or $\alpha = \{ns\ell j m_j\}$. A $N-$particle system will involve $N-$single particle wavefunctions ($\phi_i \quad i = 1, 2, \ldots, N$) and $N-$sets of single particle quantum numbers ($\alpha_k \quad k = 1, 2, \ldots, N$). The wavefunction , Ψ, for the $N-$particle system will be such that

$$\Psi = \Psi(\phi_1, \phi_2, \ldots, \phi_N) \tag{1.1}$$

For a two-particle system we could write

$$\Psi(\phi_1, \phi_2) = \frac{1}{\sqrt{2}}\{\phi_1(\alpha_1)\phi_2(\alpha_2) \pm \phi_1(\alpha_2)\phi_2(\alpha_1)\} \tag{1.2}$$

The *positive* sign corresponds to a *symmetric* wavefunction and the *minus* sign corresponds to an *antisymmetric* wavefunction. Note that we have permuted the quantum numbers with respect to the coordinates of the particles. The wavefunction of a pair of fermions, unlike a pair of bosons, undergoes a change of sign. If $\alpha_1 = \alpha_2$ then for identical fermions Eq.(1.2) vanishes though not for bosons. That is consistent with the Pauli exclusion principle for identical fermions. Thus permutational symmetry, required by the indistinguishability of identical particles, leads for $N-$fermions to the construction of of *determinantal states* to give totally *antisymmetric* states while for $N-$bosons to the construction of *permanental states* to give totally *symmetric* states. Hence for an $N-$fermion system we have the totally antisymmetric wavefunction

$$\Psi(\phi_1,\phi_2,\ldots,\phi_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_1(\alpha_1) & \phi_1(\alpha_2) & \ldots & \phi_1(\alpha_N)\\ \phi_2(\alpha_1) & \phi_2(\alpha_2) & \ldots & \phi_2(\alpha_N)\\ \vdots & \vdots & \ddots & \vdots\\ \phi_N(\alpha_1) & \phi_N(\alpha_2) & \ldots & \phi_N(\alpha_N)\end{vmatrix}^{\{1^N\}} \tag{1.3}$$

In $LS-$coupling basis we use $\alpha = \{ns\ell m_s m_\ell\}$ whereas in $jj-$coupling we would use $\alpha = \{ns\ell j m_j\}$. The information content of the determinantal state may be fully specified by the abbreviated form

$$\{\alpha_1\alpha_2\ldots\alpha_N\} \tag{1.4}$$

In the case of bosons we are required to construct permanental states to yield totally symmetric wavefunctions,

$$\Psi(\phi_1,\phi_2,\ldots,\phi_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\phi_1(\alpha_1) & \phi_1(\alpha_2) & \ldots & \phi_1(\alpha_N)\\ \phi_2(\alpha_1) & \phi_2(\alpha_2) & \ldots & \phi_2(\alpha_N)\\ \vdots & \vdots & \ddots & \vdots\\ \phi_N(\alpha_1) & \phi_N(\alpha_2) & \ldots & \phi_N(\alpha_N)\end{vmatrix}^{\{N\}} \tag{1.5}$$

The information content of the permanental state may be fully specified by the abbreviated form

$$[\alpha_1\alpha_2\ldots\alpha_N] \tag{1.6}$$

We shall use square brackets [] to indicate boson states and curly brackets { } for fermion states. Equations (1.3) and (1.6) look remarkably similar. We have distinguished them by superscripts $\{1^N\}$ and $\{N\}$, respectively. The matrix of the single particle functions are the same in both cases but the action on the matrix is different. In the first case the *determinant* of the matrix is formed and in the second the *permanent* of the matrix is formed. Could we form other objects of interest by other actions on a matrix?

1.8 Many-particle states of Bosons and Fermions

Let us for the moment consider the states of N identical bosons or fermions. Suppose the boson has an angular momentum $j = 2$ (i.e. a $d-$boson) and hence $m_j = 0, \pm1, \pm2$ while the fermion has angular momentum $j = 5/2$ and hence $m_j = \pm1/2, \pm3/2, \pm5/2$. If $N = 2$ in both cases what are the allowed values of J ? We note that

$$M_J = m_{j_1} + m_{j_2}$$

Just considering the non-negative values of M_J we obtain for the fermions the following table of determinantal states:

Table 1.1 Determinantal states for $(5/2)^2$ fermions.

M_J		States	
4	$\{5/2\,3/2\}$		
3	$\{5/2\,1/2\}$		
2	$\{5/2\ -1/2\}$	$\{3/2\,1/2\}$	
1	$\{5/2\ -3/2\}$	$\{3/2\ -1/2\}$	
0	$\{5/2\ -5/2\}$	$\{3/2\ -3/2\}$	$\{1/2\ -1/2\}$

Inspection of the above table leads to the conclusion that the allowed values of J in $(5/2)^2$ are $J = 0, 2, 4$.

The corresponding d^2 boson states for non-negative M_J are given in Table 1.2.

Table 1.2. Permanental states for d^2 bosons

M_J		States	
4	$[2\,2]$		
3	$[2\,1]$		
2	$[2\,0]$	$[1\,1]$	
1	$[2\ -1]$	$[1\,0]$	
0	$[2\ -2]$	$[1\ -1]$	$[0\,0]$

Inspection of the above table leads to the conclusion that the allowed values of J in d^2 are $J = 0, 2, 4$ exactly those found for $(5/2)^2$.*

Exercises

1.1 Show that the totally antisymmetric orbital angular momentum states of g^3 $(\ell = 4)$ (i.e. the states of maximum multiplicity) are the same as for the totally symmetric states of $(5/2)^4$.

1.2 Determine the allowed values of J for the $jj-$coupled configurations $(5/2)^2, (5/2\,7/2)$ and $(7/2)^2$.

1.3 Determine the allowed values of S and L for the electron configuration f^2.

1.4 Given that for an $LS-$coupled term ^{2S+1}L we have $\mathbf{J} = \mathbf{L} + \mathbf{S}$ and

$$J = L + S, L + S - 1, \ldots, |L - S| \tag{1.7}$$

Show that the values of J for the list of terms found in Ex 1.3. are the same as those found in Ex 1.2.

*In general the *antisymmetric* states of N identical particles each having angular $j = m/2$ and the *symmetric* states of N particles each having angular momentum $j = (m + n + 1)/2$ have the same total angular momentum J values. See B.G.Wybourne, *Hermite's reciprocity Law and the Angular Momentum States of Equivalent Particle Configurations* J.Math.Phys. **10**, 467-71 (1969).

1.5 Show that in the configuration j^2 the only allowed values of J are the even integers $0, 2, \ldots, 2j-1$.

1.6 Starting with the angular momentum commutation relations

$$[J_x, J_y] = iJ_z \quad , [J_y, J_z] = iJ_x \quad , [J_z, J_x] = iJ_y \tag{1.8}$$

show that if $J_\pm = J_x \pm iJ_y$ then

$$\mathbf{J}^2 = \frac{J_+J_- + J_-J_+}{2} + J_z^2 \tag{1.9}$$

1.7 If $\mathbf{J} = \mathbf{L} + \mathbf{S}$ show that

$$J(J+1) - L(L+1) - S(S+1) = S_+L_- + S_-L_+ + 2S_zL_z \tag{1.10}$$

Lecture Two

2.1 Ladder Operators and Determinantal States

For the electron configuration f^2 we can enumerate the set of determinantal states for non-negative M_S, M_L as in Table 2.1.

Table 2.1. Determinantal states for the Electron Configuration f^2.

M_L	$M_S = 0$	$M_S = 1$
6	$\{\overset{+}{3}\ \overset{-}{3}\}$	
5	$\{\overset{+}{3}\ \overset{-}{2}\}$ $\{\overset{+}{2}\ \overset{-}{3}\}$	$\{\overset{+}{3}\ \overset{+}{2}\}$
4	$\{\overset{+}{3}\ \overset{-}{1}\}$ $\{\overset{+}{2}\ \overset{-}{2}\}$ $\{\overset{+}{1}\ \overset{-}{3}\}$	$\{\overset{+}{3}\ \overset{+}{1}\}$
3	$\{\overset{+}{3}\ \overset{-}{0}\}$ $\{\overset{+}{2}\ \overset{-}{1}\}$ $\{\overset{+}{1}\ \overset{-}{2}\}$ $\{\overset{+}{0}\ \overset{-}{3}\}$	$\{\overset{+}{3}\ \overset{+}{0}\}$ $\{\overset{+}{2}\ \overset{+}{1}\}$
2	$\{\overset{+}{2}\ \overset{-}{0}\}$ $\{\overset{+}{3}\ \overset{-}{-1}\}$ $\{\overset{+}{1}\ \overset{-}{1}\}$ $\{\overset{+}{0}\ \overset{-}{2}\}$ $\{\overset{+}{-1}\ \overset{-}{3}\}$	$\{\overset{+}{3}\ \overset{+}{-1}\}$ $\{\overset{+}{2}\ \overset{+}{0}\}$
1	$\{\overset{+}{1}\ \overset{-}{0}\}$ $\{\overset{+}{2}\ \overset{-}{-1}\}$ $\{\overset{+}{3}\ \overset{-}{-2}\}$ $\{\overset{+}{0}\ \overset{-}{1}\}$ $\{\overset{+}{-1}\ \overset{-}{2}\}$ $\{\overset{+}{-2}\ \overset{-}{3}\}$	$\{\overset{+}{3}\ \overset{+}{-2}\}$ $\{\overset{+}{1}\ \overset{+}{0}\}$ $\{\overset{+}{2}\ \overset{+}{-1}\}$
0	$\{\overset{+}{0}\ \overset{-}{0}\}$ $\{\overset{+}{1}\ \overset{-}{-1}\}$ $\{\overset{+}{2}\ \overset{-}{-2}\}$ $\{\overset{+}{3}\ \overset{-}{-3}\}$ $\{\overset{+}{-1}\ \overset{-}{1}\}$ $\{\overset{+}{-3}\ \overset{-}{3}\}$	$\{\overset{+}{3}\ \overset{+}{-3}\}$ $\{\overset{+}{2}\ \overset{+}{-2}\}$ $\{\overset{+}{1}\ \overset{+}{-1}\}$
	$\{\overset{+}{-2}\ \overset{-}{2}\}$	

Recall that for an electron in an $f-$orbital $\ell = 3$ and hence $m_\ell = 0, \pm1, \pm2, \pm3$. There are just two values of the spin projection $m_s = \pm 1/2$. Thus it suffices in writing a determinantal state to just display the values of m_ℓ and indicate the value of m_s as a $+$ or $-$ sign placed above m_ℓ. For a given determinantal state we have

$$M_S = \sum_{i=1}^{n} m_{s_i} \qquad \text{and} \qquad M_L = \sum_{i=1}^{n} m_{\ell_i} \tag{2.1}$$

Thus every determinantal state may be associated with definite values of M_S and M_L. That does not mean that they are eigenstates of the total spin S and orbital L angular momentum. To form such eigenstates we must form appropriate linear combinations of the determinantal states to give eigenstates $|SLM_SM_L>$. Following tradition we will normally write such a state as $|^{2S+1}LM_SM_L>$ where $(2S+1)$ is known as the *spin multiplicity*. The quantum number L is usually associated with alphabetical letters

$$\begin{array}{ccccccccc} 0 & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ S & P & D & F & G & H & I & K & M \end{array}$$

A spectroscopic term will be designated as

$$^{2S+1}L$$

Associated with a given value on S there are $(2S+1)$ values of M_S and with L there are $(2L+1)$ values of M_L where

$$M_S = S, S-1, \ldots, -S+1, -S \quad \text{and} \quad M_L = L, L-1, \ldots, -L+1, -L$$

Inspection of Table 2.1 shows that the spectroscopic terms of the electron configuration f^2 are

$$^3PFH \quad ^1SDGI$$

Choose

$$|^1I06> \equiv \{\overset{+}{3}\ \overset{-}{3}\} \tag{2.2}$$

Let us now determine $|^1I05>$. To do this we use the properties of ladder operators. Recall

$$L_{\pm}|LM> = \sqrt{L(L+1)-M(M\pm 1)}|LM\pm 1> \tag{2.3}$$

and

$$L_{\pm} = \sum_{i=1}^{n} \ell_{\pm_i} \tag{2.4}$$

Let (2.3) act on the left-hand-side of (2.2) and noting (2.3) act also on the determinantal state to give

$$L_-|^1I06> = \sqrt{6\times 7 - 6\times 5}|^1I05> = \sqrt{12}|^1I05> \tag{2.5}$$

and

$$L_-\{\overset{+}{3}\ \overset{-}{3}\} = \sqrt{3\times 4 - 3\times 2}[\{\overset{+}{2}\ \overset{-}{3}\} + \{\overset{+}{3}\ \overset{-}{2}\}] \tag{2.5}$$

Equating (2.4) and (2.5) gives

$$|^1I05> = \frac{\sqrt{2}}{2}[\{\overset{+}{2}\ \overset{-}{3}\} + \{\overset{+}{3}\ \overset{-}{2}\}] \tag{2.6}$$

This state must be orthogonal to the state $|^3H05>$ and hence after fixing a phase we have

$$|^3H05> = \frac{\sqrt{2}}{2}[\{\overset{+}{2}\ \overset{-}{3}\} - \{\overset{+}{3}\ \overset{-}{2}\}] \tag{2.7}$$

Application of the spin raising operator S_+ to (2.7) gives

$$S_+|^3H05> = \sqrt{2}|^3H15> = \frac{\sqrt{2}}{2}[\{\overset{+}{2}\ \overset{+}{3}\} - \{\overset{+}{3}\ \overset{+}{2}\}]$$

and hence

$$|^3H15> = -\{\overset{+}{3}\ \overset{+}{2}\}] \tag{2.8}$$

Note the appearance of the minus sign which comes from our particular choice of enumeration of the determinantal states.

Exercises

2.1 Determine the eigenstates

$$|^1I04> \quad |^3H04> \quad |^1G04> \quad |^3H14>$$

as linear combinations of determinantal states.

2.2 Discuss how you could determine the eigenstates $|^3HJM>$ as linear combinations of the states $|^3HM_SM_L>$. *Hint*: use the fact that $J_\pm = L_\pm + S_\pm$.

2.2 Permutations and the Symmetric Group

Permutations play an important role in the physics of identical particles. A permutation leads to a reordering of a sequence of objects. We can place n objects in the natural number ordering $1, 2, \ldots, n$. Any other ordering can be discussed in terms of this ordering and can be specified in a two line notation

$$\begin{matrix} 1 & 2 & \ldots & n \\ \pi(1) & \pi(2) & \ldots & \pi(n) \end{matrix} \tag{2.9}$$

For $n = 3$ we have the six permutations

$$\begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} \tag{2.10}$$

Permutations can be multiplied working from right to left. Thus

$$\begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix} \times \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix}$$

In this example we see that the two permutations on the left are inverses of each other. The result has been the identity permutation.
The six permutations in (2.10) satisfy the following properties:

1. There is an identity element $\begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix}$.
2. Every element has an inverse among the set of elements.
3. The product of any two elements yields elements of the set.
4. The elements satisfy the associativity condition a(bc) = (ab)c. These conditions establish that the permutations form a group. In general the $n!$ permutations form the elements of the symmetric group $\mathcal{S}_n$.

2.3 Cycle Structure of Permutations

It is useful to express permutations as a cycle structure. A cycle $(i, j, k, \ldots, l)$ is interpreted as $i \to j$, $j \to k$ and finally $l \to i$. Thus our six permutations have the cycle structures

$$(1)(2)(3), \qquad (1,2)(3), \qquad (1)(2,3), \qquad (1,3)(2), \qquad (1,3,2), \qquad (1,2,3) \tag{2.11}$$

Note that the elements within a cycle can be cyclically permuted and that the order of the cycles is irrelevant. Thus $(123)(45) \equiv (54)(312)$.
A $k-$*cycle* or *cycle of length* k contains k elements. For reasons that will shortly become apparent it is useful to organise cycles into *types* or *classes*. We shall designate the *cycle type* of a permutation π by

$$(1^{m_1}\, 2^{m_2}\, \ldots, n^{m_n}) \tag{2.12}$$

where m_k is the number of cycles of length k in the cycle representation of the permutation π. Thus for the case of $\mathcal{S}_4$ we have the five cycle types

$$(1^4),\ (1^2\, 2^1),\ (2^2),\ (1^1\, 3^1),\ (4^1) \tag{2.13}$$

Without confusion we will normally omit exponents of unity and write Eq.(2.13) more simply as

$$(1^4),\ (1^2\, 2),\ (2^2),\ (1\, 3),\ (4) \tag{2.14}$$

Cycle types may be equally well labelled by ordered partitions of the integer n

$$\lambda = (\lambda_1\, \lambda_2\, \ldots\, \lambda_\ell) \tag{2.15}$$

where the λ_i are weakly decreasing and

$$\sum_{i=1}^{\ell} \lambda_i = n \tag{2.16}$$

The partition is said to be of *length* ℓ and of *weight* n. In terms of partitions we have the cycle types for $\mathcal{S}_5$

$$(1^5),\ (2\, 1^3),\ (2^2\, 1),\ (3\, 2),\ (3\, 1^2),\ (4\, 1),\ (5)$$

2.4 Conjugacy Classes of $\mathcal{S}_n$

In any group G we say the elements g and h are *conjugates* if

$$g = k\, h\, k^{-1} \qquad \text{for some} \qquad k \in G \tag{2.17}$$

The set of all elements conjugate to a given g is call the *conjugacy class* of g which we denote as K_g.

Exercises

2.3 Show that for $\mathcal{S}_4$ there are five conjugacy classes that may be labelled by the five partitions of the integer 4.

2.4 Show that the permutations, expressed in cycles with cycles of length one suppressed, divide among the conjugacy classes as

$$\begin{aligned} (1^4) &\supset e \\ (2\,1^2) &\supset (1\,2),\ (1\,3),\ (1\,4),\ (2\,3),\ (2\,4),\ (3\,4) \\ (2^2) &\supset (1\,2)(3\,4),\ (1\,3)(2\,4),\ (1\,4)(2\,3) \\ (3\,1) &\supset (1\,2\,3),\ (1\,2\,4),\ (1\,3\,2),\ (1\,3\,4),\ (1\,4\,2),\ (1\,4\,3),\ (2\,3\,4),\ (2\,4\,3) \\ (4) &\supset (1\,2\,3\,4),\ (1\,2\,4\,3),\ (1\,3\,4\,2),\ (1\,4\,3\,2) \end{aligned} \tag{2.18}$$

From the preceding exercise we can show in general two permutations are in the same conjugacy class if, and only if, they are of the same cycle type. The number of classes of $\mathcal{S}_n$ is equal the number of partitions of the integer n.
If $\lambda = (1^{m_1}\, 2^{m_2}\, \ldots\, n^{m_n})$ then the number of permutations k_λ in the class (λ) of $\mathcal{S}_n$ is

$$k_\lambda = \frac{n!}{1^{m_1}\, m_1!\, 2^{m_2}\, m_2!\, \ldots\, n^{m_n}\, m_n!} \tag{2.19}$$

2.5 The Alternating Group $\mathcal{A}_n$

A cycle of order two is termed a *transposition*. A transposition $(i,\ i+1)$ is termed an *adjacent transposition*. The entire symmetric group $\mathcal{S}_n$ can be generated (or given a *presentation* in terms of the set of adjacent transpositions

$$(1\,2),\ (2\,3),\ \ldots,\ (n-1\,n) \tag{2.20}$$

If $\pi = \tau_1 \tau_2 \ldots \tau_k$, where the τ_i are transpositions then the *sign* of π is defined to be

$$sgn(\pi) = (-1)^k \tag{2.21}$$

If the number of cycles of *even* order is *even* then the permutation is *even* or *positive*; if it is *odd* then the permutation is *odd* or *negative*.
The set of *even* permutations form a subgroup of $\mathcal{S}_n$ known as the *alternating group* $\mathcal{A}_n$ and has precisely half the elements of $\mathcal{S}_n$ i.e. $(\frac{1}{2})n!$.

Exercises

2.5 Show that the set of six matrices

$$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 0 & 1 \\ -1 & -1 \end{bmatrix} \begin{bmatrix} -1 & -1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \begin{bmatrix} -1 & -1 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ -1 & -1 \end{bmatrix} \tag{2.22}$$

with the usual rule of matrix multiplication form a group isomorphic to $\mathcal{S}_3$.

2.6 Show that the symmetric group $\mathcal{S}_n$ has two one-dimensional representations, a symmetric representation where every element is mapped onto unity and an antisymmetric representation where the elements are mapped onto the sign defined in Eq. (2.21).

Some Relevant Literature

The following references have been chosen to give a general background to the literature relevant to this course. I shall at various times refer to them by number.

References

1. G. R. E. Black, R. C. King, and B. G. Wybourne, *Kronecker products for compact semisimple Lie groups*, J. Phys. A:Math.Gen. **16**, 1555–1589 (1983).
2. E. Cartan, *Sur la Structure des Groupes de Transformation Finis et Continus*, Thesis, Nony, Paris 1894.
3 E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra*, Cambridge University Press, Cambridge, 1935.
4. A. R. Edmonds, *Angular Momentum in Quantum Mechanics*, Princeton University Press, Princeton, 1957.
5. S. A. Fulling, R. C. King ,B. G. Wybourne and C. J. Cummins, *Normal Forms for Tensor Polynomials I. The Riemann Tensor* J. Classical and Quantum Gravitation
6. J. S. Griffith, *The Theory of the Transition Metal Ions*, Cambridge University Press, Cambridge, 1961.
7. J. S. Griffith, *The Irreducible Tensor Method for Molecular Symmetry Groups*, Prentice–Hall, Englewood Cliffs, NJ. 1962.
8. M. Hamermesh, *Group Theory and its Application to Physical Problems*, Addison–Wesley, Reading, Mass., 1962.
9. G. D. James and A. Kerber, *The Representation Theory of the Symmetric Group*, Addison–Wesley, Reading, Mass., 1981.
10. B. R. Judd, *Optical intensities of rare-earth ions*, Phys. Rev. **127** 750–61 (1962).
11. B. R. Judd, *Operator Techniques in Atomic Spectroscopy*, McGraw–Hill,New York, (1963).
12. B. R. Judd, *Second Quantization and Atomic Spectroscopy* Johns Hopkins University Press, Baltimore, Md., 1967.
13. R. C. King, *Branching rules for classical Lie groups using tensor and spinor methods*, J. Phys. A:Math.Gen. **8**, 429–449 (1975).
14. R. C. King and A. H. A. Al-Qubanchi, *Natural labelling schemes for simple roots and irreducible representations of exceptional Lie algebras*, J. Phys. A:Math.Gen. **14** 15–49 (1981).
15. R. C. King and A. H. A. Al-Qubanchi, *The Weyl groups and weight multiplicities of the exceptional groups*, J. Phys. A:Math.Gen. **14** 51–75 (1981).
16. R. C. King, *Kronecker products of representations of exceptional Lie groups*, J. Phys. A:Math.Gen. **14** 77–83 (1981).
17. R. C. King, Luan Dehuai and B. G. Wybourne, *Symmetrised powers of rotation group representations*, J. Phys. A:Math.Gen. **14**, 2509–38 (1981).

18. D. E. Littlewood, *The Theory of Group Characters and Matrix Representations of Groups*, 2nd ed., Clarendon Press, Oxford, 1950.
19. D. E. Littlewood, *Invariant theory, tensors and group characters*, Phil. Transac. Roy. Soc. (London) **A239**, 305–365 (1944).
20. D. E. Littlewood, *On invariant theory under restricted groups*, Phil. Transac. Roy. Soc. (London) **A239**, 387–417 (1944).
21. D. E. Littlewood, *On the concomitants of spin tensors*, Proc. London Math. Soc. (2), **49**, 307–27 (1947).
22. D. E. Littlewood, *Invariant theory under orthogonal groups*, Proc. London Math. Soc. (2), **50**, 406–13 (1948).
23. D. E. Littlewood and A. R. Richardson, *Group characters and algebra*, Phil. Transac. Roy. Soc. (London) **A233**, 99–141 (1934).
24. I. G. Macdonald, *Symmetric Functions and Hall Polynomials*, Clarendon Press, Oxford, 1979.
25. A. Messiah, *Quantum Mechanics*, Vol. 2, North-Holland, Amsterdam, 1961, Appendix D.
26. F. D. Murnaghan, *The Theory of Group Representations*, Johns Hopkins University Press, Baltimore, Md., 1938.
27. C. W. Nielson and G. F. Koster, *Spectroscopic coefficients for the p^n, d^n and f^n Configurations*, MIT Press, Cambridge, Mass. 1963.
28. G. S. Ofelt, *Intensities of crystal spectra of rare-earth ions*, J. Chem. Phys. **37** 511–20 (1962).
29. G. Racah, *Theory of Complex Spectra I*, Phys. Rev. **61** 186–97 (1942).
30. G. Racah, *Theory of Complex Spectra II*, Phys. Rev. **62** 438–62 (1942).
31. G. Racah, *Theory of Complex Spectra III*, Phys. Rev. **63** 367–82 (1943).
32. G. Racah, *Theory of Complex Spectra IV*, Phys. Rev. **76**, 1352–65 (1949).
33. G. Racah, *Group Theory and Spectroscopy*, Springer Tracts in Modern Physics Vol. **37**, edited by G. Höhler (Springer-Verlag, Berlin 1965.
34. G. de B. Robinson, *Representation Theory of the Symmetric Group*, Edinburgh University Press, Edinburgh, 1961.
35. D. E. Rutherford, *Substitutional Analysis*, Edinburgh University Press, Edinburgh, 1948.
36. B. E. Sagan, *The Symmetric Group*, Wadsworth & Brooks/Cole Cal. 1991.
37. H. Watanabe, *Operator Methods in Ligand Field Theory*, Prentice–Hall, Englewood Cliffs, NJ. 1966.
38. H. Weyl, *Gruppentheorie und Quantenmechanik* S. Hirzel, Leipzig, 1931. Translated by H.P.Robertson *The Theory of Groups and Quantum Mechanics* , Dover, New York, 1950.

39. H. Weyl, *The Classical Groups*, Princeton University Press, Princeton, 1939.
40. B. G. Wybourne, *Spectroscopic Properties of Rare Earths*, Wiley, New York, 1965.
41. B. G. Wybourne, *Symmetry Principles and Atomic Spectroscopy*, Wiley, New York, 1970.
42. B. G. Wybourne, *Classical Groups for Physicists*, Wiley, New York, 1974.

Symmetry and Spectroscopic Calculations

Lecture Three

3.1 Properties of Symmetric Functions

In this, and the following, lecture we seek to explore some of the properties of symmetric functions and in particular to try to develop generalisations of the determinants and permanents leading to the Schur functions and the immanants of matrices of which the determinants and permanents are special cases. Here we follow the definitive notation outline by Macdonald[24].

3.2 Partitions

Partitions play a key role in much of the following. We shall take a partition as any finite or infinite sequence integers

$$\lambda = (\lambda_1\, \lambda_2\, \ldots\, \lambda_i\, \ldots) \tag{3.1}$$

Unless otherwise stated we shall assume the sequence involves non-negative integers in non-increasing order;

$$\lambda_1 \geq \lambda_2 \geq \ldots \geq \lambda_i \geq \ldots \tag{3.2}$$

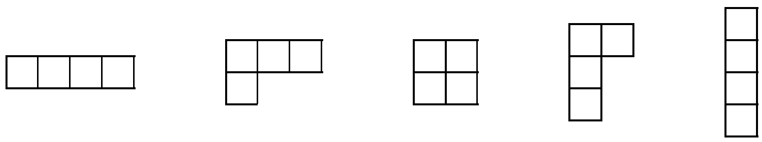
Normally we will omit zeros. The non-zero λ_i form the *parts* of λ. The number of parts is the *length*, $\ell(\lambda)$, of λ while the sum of its parts, $|\lambda|$, is the *weight* of λ. If $|\lambda| = n$ then λ is said to be a *partition* of n. We shall frequently write $\lambda \vdash n$ to indicate that λ is a partition of n. Repeated parts of a partition will frequently be indicated as i^{m_i} where m_i is the number of times the part i occurs in the partition λ. Thus we shall write the partitions for $n = 6$ as

$$(6)\,(51)\,(42)\,(41^2)\,(3^2)\,(321)\,(31^3)\,(2^3)\,(2^21^2)\,(21^4)\,(1^6)$$

Note, in the above example the partitions have been listed in *reverse lexicographic order.* The ordering is such that the first non-vanishing difference $\lambda_i - \mu_i$, for successive partitions λ, μ is *positive.*

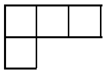
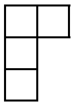
3.2 The Ferrers-Sylvester diagram

Every partition $\lambda \vdash n$ may be associated with a *Ferrers-Sylvester diagram, shape* or *frame* involving n cells, dots or boxes in $\ell(\lambda)$ left-adjusted rows with the i-th row containing λ_i cells, dots, or boxes. Thus for $n = 4$ we have the five diagrams

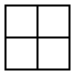


We will formally designate the frame associated with a partition λ as F^λ.

The *conjugate* of a partition λ is a partition λ' whose diagram is the transpose of the diagram of λ. If $\lambda' \equiv \lambda$ then the partition λ is said to be *self-conjugate*. Thus

 and 

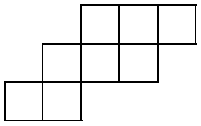
are conjugates while



is self-conjugate.

3.3 Skew frames

Given two partitions λ and μ such that $\lambda \supset \mu$ implies that the frame F^λ contains the frame F^μ, i.e. that $\lambda_i \geq \mu_i$ for all $i \geq 1$. The difference $\rho = \lambda - \mu$ forms a *skew* frame $F^{\lambda/\mu}$. Thus, for example, the skew frame $F^{542/21}$ has the form



Note that a skew frame may consist of disconnected pieces.

3.4 Frobenius notation for partitions

There is an alternative notation for partitions due to Frobenius. The *diagonal* of nodes in a Ferrers-Sylvester diagram beginning at the top left-hand corner is called the *leading diagonal*. The number of nodes in the leading diagonal is called the *rank* of the partition. If r is the rank of a partition then let a_i be the number of nodes to the right of the leading diagonal in the $i-$th row and let b_i be the number of nodes below the leading diagonal in the $i-$th column. The partition is then denoted by Frobenius as

$$\begin{pmatrix} a_1, & a_2, & \ldots, & a_r \\ b_1, & b_2, & \ldots, & b_r \end{pmatrix} \tag{3.3}$$

We note that

$$a_1 > a_2 > \ldots > a_r$$
$$b_1 > b_2 > \ldots > b_r$$

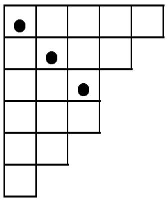
and

$$a_1 + a_2 + \ldots + a_r + b_1 + b_2 + \ldots + b_r + r = n$$

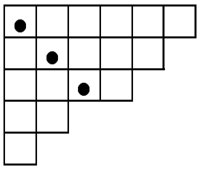
The partition conjugate to that of Eq.(3.3) is just

$$\begin{pmatrix} b_1, & b_2, & \ldots, & b_r \\ a_1, & a_2, & \ldots, & a_r \end{pmatrix} \tag{3.4}$$

As an example consider the partitions $(5\,4\,3^2\,2\,1)$ and $(6\,5\,4\,2\,1)$. Drawing their diagrams and marking their leading diagonal we have



and



from which we deduce the respective Frobenius designations

$$\begin{pmatrix} 4 & 2 & 0 \\ 5 & 3 & 1 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 5 & 3 & 1 \\ 4 & 2 & 0 \end{pmatrix}$$

3.5 Young tableaux

A Young tableau is an assignment of n numbers to the n cells of a frame F^λ with $\lambda \vdash n$ according to some numbering sequence. A tableau is *standard* if the assignment of the numbers $1, 2, \ldots, n$ is such that the numbers are positively increasing from left to right in rows and down columns from top to bottom. Thus for the partitions of the integer 4 we have the standard Young tableaux

$$\begin{array}{|c|c|c|c|}\hline 1&2&3&4\\\hline\end{array}$$

$$\begin{array}{|c|c|c|}\hline 1&2&3\\\hline 4\\\cline{1-1}\end{array} \qquad \begin{array}{|c|c|c|}\hline 1&2&4\\\hline 3\\\cline{1-1}\end{array} \qquad \begin{array}{|c|c|c|}\hline 1&3&4\\\hline 2\\\cline{1-1}\end{array}$$

$$\begin{array}{|c|c|}\hline 1&2\\\hline 3&4\\\hline\end{array} \qquad \begin{array}{|c|c|}\hline 1&3\\\hline 2&4\\\hline\end{array}$$

$$\begin{array}{|c|c|}\hline 1&2\\\hline 3\\\cline{1-1} 4\\\cline{1-1}\end{array} \qquad \begin{array}{|c|c|}\hline 1&3\\\hline 2\\\cline{1-1} 4\\\cline{1-1}\end{array} \qquad \begin{array}{|c|c|}\hline 1&4\\\hline 2\\\cline{1-1} 3\\\cline{1-1}\end{array}$$

$$\begin{array}{|c|}\hline 1\\\hline 2\\\hline 3\\\hline 4\\\hline\end{array}$$

We notice in the above examples that the number of standard tableaux for conjugate partitions is the same. Indeed the number of standard tableaux associated with a given frame F^λ is the *dimension* f_n^λ of an irreducible representation $\{\lambda\}$ of the symmetric group $\mathcal{S}_n$.

3.6 Hook lengths and dimensions for $\mathcal{S}_n$

The *hook length* of a given box in a frame F^λ is the length of the right-angled path in the frame with that box as the upper left vertex. For example, the hook length of the marked box in

$$\begin{array}{ccccc} \square & \square & \square & \square & \square \\ * & \cdot & \cdot & \cdot & \\ \cdot & \square & \square & & \\ \cdot & \square & \square & & \\ \cdot & \square & & & \\ \cdot & & & & \end{array}$$

is 8.

Theorem 3.1: *To find the dimension of the representation of $\mathcal{S}_n$ corresponding to the frame F^λ, divide $n\,!$ by the factorial of the hook length of each box in the first column of F^λ and multiply by the difference of each pair of such hook lengths.*

Thus for the partition $(5\,4\,3^2\,2\,1)$ we have the hook lengths

$$\begin{array}{ccccc} 10 & \square & \square & \square & \square \\ 8 & \square & \square & \square & \\ 6 & \square & \square & & \\ 5 & \square & \square & & \\ 3 & \square & & & \\ 1 & & & & \end{array}$$

and hence a dimension

$$\begin{aligned} f_{18}^{543^2 21} &= 18\,! \frac{2\times 4\times 5\times 7\times 9\times 2\times 3\times 5\times 7\times 1\times 3\times 5\times 2\times 4\times 2}{10\,!\times 8\,!\times 6\,!\times 5\,!\times 3\,!\times 1\,!} \\ &= 10720710 \end{aligned}$$

It is not suggested that you check the above result by explicit enumeration! The above evaluation can also be equivalently made by computing the hook lengths h_{ij} for every box at position (i,j) and then noting that

$$f_n^\lambda = \frac{n\,!}{\prod_{(i,j)\in\lambda} h_{ij}} \tag{3.5}$$

which is the celebrated result of Frame, Robinson and Thrall.

Exercises

3.1 Show that the dimension of of the representation*

$$\{p+2,2\} = \begin{array}{cccccccc} \square & \square & \square & \square & \square & \cdots & \square & \square \\ \square & \square & & & & & & \end{array}$$

*This is in fact the number of independent index orders of the differentiated Riemann tensor, $\nabla^p R$, when the noncommutativity of covariant derivatives is ignored[5].

is

$$\frac{1}{2}(p+4)(p+1)$$

3.2 Calculate the dimensions of the irreducible representations of $\mathcal{S}_6$ and show that**

$$\sum_{\lambda \vdash 6} (f_6^\lambda)^2 = 6\,!$$

3.7 The symmetric group and tensors

While it is not our intention here to develop the detailed connection between Young tableaux and tensors in detail the connection is too important to totally ignore. For more details you should consult the literature[5,8,19,39].

Let $T_{\mu_1 \ldots \mu_n}$ be a "generic" n-index tensor, without any special symmetry. (For the moment, "tensor" means just a function of n indices, not necessarily with any geometrical realization. It must be meaningful, however, to *add* (and form linear combinations of) tensors of the same rank.)

The entries $1, 2, \ldots n$ in the standard numbering of a tableau indicate the n successive indices of $T_{\mu_1 \cdots \mu_n}$. The tableau defines a certain symmetrization operation on these indices: *symmetrize* on the set of indices indicated by the entries in each row, then *antisymmetrize* the result on the set of indices indicated by the entries in each column. The resulting object is a tensor, T, with certain index symmetries. Now let each permutation in S_n act (separately) upon T. The $n!$ results are not linearly independent; they span a vector space which supports an irreducible representation of S_n. Different tableaux corresponding to the same frame yield equivalent (but not identical) representations.

Example: The partition $\{2\,2\}$ of 4 has two standard tableaux:

$$\begin{array}{|c|c|}\hline 1 & 2 \\ \hline 3 & 4 \\ \hline \end{array} \quad \text{and} \quad \begin{array}{|c|c|}\hline 1 & 3 \\ \hline 2 & 4 \\ \hline \end{array} \tag{3.6}$$

Let us construct the symmetrized tensor T corresponding to the second of these. First symmetrize over the first and third indices, and over the second and fourth:

$$\frac{1}{4}\left(T_{abcd} + T_{cbad} + T_{adcb} + T_{cdab}\right).$$

**This is an example of the general result that

$$\sum_{\lambda \vdash n} (f_n^\lambda)^2 = n\,!$$

Now antisymmetrize the result over the first and second indices, and the third and fourth; dropping the combinatorial factor $\frac{1}{16}$, we get

$$\begin{aligned} T_{abcd} = {} & T_{abcd} + T_{cbad} + T_{adcb} + T_{cdab} \\ & - T_{bacd} - T_{cabd} - T_{bdca} - T_{cdba} \\ & - T_{abdc} - T_{dbac} - T_{acdb} - T_{dcab} \\ & + T_{badc} + T_{dabc} + T_{bcda} + T_{dcba} \,. \end{aligned} \tag{3.7}$$

It is easy (though tedious) to check that T possesses the symmetries characteristic of the Riemann tensor. There are two independent orders of its indices, and applying any permutation to the indices produces some linear combination of those two basic objects. On the other hand, performing on T the operations prescribed by the first tableau in (3.6) produces a different expression, which, however, generates a 2-dimensional representation of S_4 with the same abstract structure as that generated by T. A nonstandard tableau would also yield such a representation, but the tensors within it would be linear combinations of those already found.

Remark: In (3.7) we have adopted the convention that the second round of permutations interchanges indices with the same *names*, rather than indices in the same *positions* in the various terms. The opposite convention is tantamount to antisymmetrizing *first*, which leads to a different, but mathematically isomorphic, development of the representation theory (see Ref. 19 , pp312–314). The issue here is analogous to the distinction between space-fixed and body-fixed axes in the study of the rotation group.

Exercise

3.3 Construct a set of three 4-index tensors corresponding to the three Young tableaux associated with the partition $\{3\,1\}$.

3.8 Unitary numbering of Young tableaux

Many different prescriptions can be given for injecting numbers into the boxes of a frame. We have already noted the standard numbering which is intimately associated with the symmetric group $\mathcal{S}_n$. Another important numbering prescription is that of *unitary* numbering where now numbers 1, 2, …, d are injected into the boxes of a frame F^{λ} such that:

i. Numbers are non-decreasing across a row going from left to right.

ii. Numbers are positively increasing in columns from top to bottom.

The first condition permits repetitions of integers. Thus using the numbers 1, 2, 3 in the frame $F^{2\,1}$ we obtain the 8 tableaux

$$\begin{array}{|c|c|}\hline 1&1\\\hline 2\\\cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 1&1\\\hline 3\\\cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 1&2\\\hline 2\\\cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 1&2\\\hline 3\\\cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 1&3\\\hline 2\\\cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 1&3\\\hline 3\\\cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 2&2\\\hline 3\\\cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 2&3\\\hline 3\\\cline{1-1}\end{array} \tag{3.8}$$

Had we chosen $d = 2$ we would have obtained just two tableaux while $d = 4$ yields twenty tableaux. In general, for a frame F^λ a unitary numbering using the integers 1, 2, ..., d leads to

$$f_d^\lambda = \frac{G_d^\lambda}{H_\lambda} \tag{3.9}$$

where H_λ is the product of the hook lengths h_{ij} of the frame and

$$G_d^\lambda = \prod_{(i,j)\in\lambda} (d+i-j) \tag{3.10}$$

Thus for $d = 5$ and $\lambda = (4\,2\,1)$ we have $H_{(4\,2\,1)} = 144$ and $G_5^{\{4\,2\,1\}} = 100800$ from which we deduce that

$$f_5^{\{4\,2\,1\}} = 700$$

which is the dimension of the irreducible representation $\{4\,2\,1\}$ of the general linear group $GL(5)$. In general, f_d^λ is the dimension of the irreducible representation $\{\lambda\}$ of $GL(d)$. Since the representations of $GL(d)$ labelled by partitions λ remain irreducible under restriction to the unitary group $U(d)$ Eq.(3.9) is valid for computing the dimensions of the irreducible representations of the unitary group $U(d)$.

The same rules for a unitary numbering may be applied to the skew frames $F^{\lambda/\mu}$ introduced in §3.3. Thus for $F^{542/21}$ an allowed unitary numbering using just the integers 1 and 2 would be

$$\begin{array}{ccccc} & & \boxed{1} & \boxed{1} & \boxed{1} \\ & \boxed{1} & \boxed{2} & \boxed{2} & \\ \boxed{1} & \boxed{2} & & & \end{array}$$

Note that our unitary numbering yields what in the mathematical literature are commonly referred to as *semistandard* Young tableaux. Other numberings are possible and have been developed for all the classical Lie algebras.

Exercises

3.4 Draw the frames $F^{2^2/1}$, $F^{43^21/421^2}$, and $F^{321/21}$.

3.5 Use the integers 1, 2, 3 to construct the complete set of semistandard tableaux for the frame $F^{43^21/421^2}$ and show that the same number of tableaux arise for the frame F^{21}.

3.6 Make a similar unitary numbering for the frame $F^{321/21}$ and show that the same number of semistandard tableaux arise in the set of frames $F^3 + 2F^{21} + F^{1^3}$.

Symmetry and Spectroscopic Calculations

Lecture Four

4.1 Young tableaux and monomials

A numbered frame may be associated with a unique monomial by replacing each integer i by a variable x_i. Thus the Young tableau

$$\begin{array}{|c|c|c|c|c|}\hline 1&1&2&4&5\\ \hline 3&3&3&5\\ \cline{1-4} 4&6&7\\ \cline{1-3} 5&7&8\\ \cline{1-3} 6&8\\ \cline{1-2} 7\\ \cline{1-1}\end{array}$$

can be associated with the monomial $x_1^2\, x_2\, x_3^3\, x_4^2\, x_5^3\, x_6^2\, x_7^3\, x_8^2$

4.2 Monomial symmetric functions

Consider a set of variables $(x) = x_1, x_2, \ldots, x_d$. A *symmetric* monomial

$$\boxed{\boxed{m_\lambda(x) = \sum_\alpha x^\alpha}} \tag{4.1}$$

involves a sum over all distinct permutations α of $(\lambda) = (\lambda_1, \lambda_2, \ldots)$. Thus if $(x) = (x_1, x_2, x_3)$ then

$$\begin{aligned} m_{21}(x) &= x_1^2\, x_2 + x_1^2\, x_3 + x_1\, x_2^2 + x_1\, x_3^2 + x_2^2\, x_3 \\ m_{1^3}(x) &= x_1\, x_2\, x_3 \end{aligned}$$

The unitary numbering of $(\lambda) = (2\,1)$ with 1, 2, 3 corresponds to the sum of monomials

$$\boxed{\boxed{m_{21}(x) + 2m_{1^3}(x)}}$$

The same linear combination occurs for any number of variables* with $d \geq 3$.
The monomials $m_\lambda(x)$ are *symmetric functions.* If $\lambda \vdash n$ then $m_\lambda(x)$ is homogeneous of degree n. Unless otherwise stated we shall henceforth assume that x involves an infinite number of variables x_i.
The *ring of symmetric functions* $\Lambda = \Lambda(x)$ is the vector space spanned by all the $m_\lambda(x)$. This space can be decomposed as

$$\Lambda = \oplus_{n \geq 0} \Lambda^n \tag{4.2}$$

*For two variables just $m_{21}(x)$ survives while in terms of a single variable neither monomial survives.

where Λ^n is the space spanned by all m_λ of degree n. Thus the $\{m_\lambda | \lambda \vdash n\}$ form a basis for the space Λ^n which is of dimension $p(n)$ where $p(n)$ is the number of partitions of n. It is of interest to ask if other bases can be constructed for the space Λ^n.

4.3 The classical symmetric functions

Three other classical bases are well-known - some since the time of Newton.

1. **The elementary symmetric functions**
   The $n-$th elementary symmetric function e_n is the sum over all products of n distinct variables x_i, with $e_0 = 1$ and generally

$$e_n = m_{1^n} = \sum_{i_1 < i_2 \ldots < i_n} x_{i_1}\, x_{i_2}\, \ldots\, x_{i_n} \tag{4.3}$$

   The *generating function* for the e_n is

$$E(t) = \sum_{n \geq 0} e_n t^n = \prod_{i \geq 1} (1 + x_i t) \tag{4.4}$$

2. **The complete symmetric functions**
   The $n-$th complete or *homogeneous* symmetric function h_n is the sum of all monomials of total degree n in the variables $x_1,\, x_2,\, \ldots$, with $h_0 = 1$ and generally

$$h_n = \sum_{|\lambda| = n} m_\lambda = \sum_{i_1 \leq i_2 \ldots \leq i_n} x_{i_1}\, x_{i_2}\, \ldots\, x_{i_n} \tag{4.5}$$

   The generating function for the h_n is

$$H(t) = \sum_{n \geq 0} h_n t^n = \prod_{i \geq 1} (1 - x_i t)^{-1} \tag{4.6}$$

3. **The power sum symmetric function**
   The $n-$th power sum symmetric function is

$$p_n = m_n = \sum_{i \geq 1} x_i^n \tag{4.7}$$

   The generating function for the p_n is

$$\begin{aligned} P(t) = \sum_{n \geq 1} p_n t^{n-1} &= \sum_{i \geq 1} \sum_{n \geq 1} x_i^n t^{n-1} \\ &= \sum_{i \geq 1} \frac{x_i}{1 - x_i t} \\ &= \sum_{i \geq 1} \frac{d}{dt} \log \frac{1}{1 - x_i t} \end{aligned} \tag{4.8}$$

and hence

$$
\begin{aligned}
P(t) &= \frac{d}{dt}\log\prod_{i\geq 1}(1-x_i t)^{-1} \\
&= \frac{d}{dt}\log H(t) \\
&= H^{'}(t)/H(t)
\end{aligned}
\tag{4.9}
$$

Similarly,

$$
P(-t) = \frac{d}{dt}\log E(t) = E^{'}(t)/E(t) \tag{4.10}
$$

Equation (4.9) leads to the relationship

$$
nh_n = \sum_{r=1}^{n} p_r\, h_{n-r} \tag{4.11}
$$

It follows from (4.9) that

$$
\begin{aligned}
H(t) &= \exp\sum_{n\geq 1} p_n\, t^n/n \\
&= \prod_{n\geq 1}\exp(p_n\, t^n/n) \\
&= \prod_{n\geq 1}\sum_{m_n=0}^{\infty}(p_n\, t^n)^{m_n}/n^{m_n}.m_n!
\end{aligned}
\tag{4.12}
$$

and hence

$$
H(t) = \sum_{\lambda} z_\lambda^{-1} p_\lambda\, t^{|\lambda|} \tag{4.13}
$$

where

$$
z_\lambda = \prod_{i\geq 1} i^{m_i}.m_i! \tag{4.14}
$$

where $m_i = m_i(\lambda)$ is the number of parts of λ equal to i. Defining

$$
\varepsilon_\lambda = (-1)^{|\lambda|-\ell(\lambda)} \tag{4.15}
$$

we can show in an exactly similar manner to that of Eq.(4.13) that

$$
E(t) = \sum_{\lambda} \varepsilon_\lambda z_\lambda^{-1} p_\lambda\, t^{|\lambda|} \tag{4.16}
$$

It then follows from Eqs.(4.13) and (4.16) that

$$h_n = \sum_{|\lambda|=n} z_\lambda^{-1} p_\lambda \tag{4.17}$$

and

$$e_n = \sum_{|\lambda|=n} \varepsilon_\lambda z_\lambda^{-1} p_\lambda \tag{4.18}$$

Exercises

4.1 Show that for $n = 3$

$$\begin{aligned} p_3 &= x_1^3 + x_2^3 + x_3^3 + \ldots \\ e_3 &= x_1\, x_2\, x_3 + x_1\, x_2\, x_4 + x_2\, x_3\, x_4 + \ldots \\ h_3 &= x_1^3 + x_2^3 + \ldots + x_1^2\, x_2 + x_1\, x_2^2 + \ldots + x_1\, x_2\, x_3 + x_1\, x_2\, x_4 + \ldots \end{aligned} \tag{4.19}$$

4.2 Noting Eqs. (4.4) and (4.6) and that $H(t)E(-t) = 1$, show that

$$\sum_{r=0}^{n} (-1)^r h_{n-r}\, e_r = 0 \tag{4.20}$$

for $n \geq 1$.

4.3 Use Eq.(4.20) to show that

$$e_n = det(h_{1-i+j})_{1\leq i,j\leq n} \tag{4.21}$$

and hence

$$h_n = det(e_{1-i+j})_{1\leq i,j\leq n} \tag{4.22}$$

4.4 Use Eq.(4.11) to obtain the determinantal expressions

$$p_n = \begin{vmatrix} e_1 & 1 & 0 & \dots & 0 \\ 2e_2 & e_1 & 1 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \\ ne_n & e_{n-1} & e_{n-2} & \dots & e_1 \end{vmatrix} \tag{4.23}$$

$$n!e_n = \begin{vmatrix} p_1 & 1 & 0 & \dots & 0 \\ p_2 & p_1 & 2 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \\ p_{n-1} & p_{n-2} & . & \dots & n-1 \\ p_n & p_{n-1} & . & \dots & p_1 \end{vmatrix} \tag{4.24}$$

$$(-1)^{n-1}p_n = \begin{vmatrix} h_1 & 1 & 0 & \dots & 0 \\ 2h_2 & h_1 & 1 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \\ nh_n & h_{n-1} & h_{n-2} & \dots & h_1 \end{vmatrix} \tag{4.25}$$

$$n!h_n = \begin{vmatrix} p_1 & -1 & 0 & \dots & 0 \\ p_2 & p_1 & -2 & \dots & 0 \\ \vdots & \vdots & \vdots & \vdots & \\ p_{n-1} & p_{n-2} & . & \dots & -n+1 \\ p_n & p_{n-1} & . & \dots & p_1 \end{vmatrix} \tag{4.26}$$

4.4 Multiplicative bases for Λ^n

The three types of symmetric functions, h_n, e_n, p_n, do not have enough elements to form a basis for Λ^n, there must be one function for every partition $\lambda \vdash n$. To that end in each case we form *multiplicative* functions f_λ so that for each $\lambda \vdash n$

$$f_\lambda = f_{\lambda_1} f_{\lambda_2} \dots f_{\lambda_\ell} \tag{4.27}$$

where $f = e,\ h,$ or p Thus, for example,

$$e_{21} = e_2 \cdot e_1 = (x_1\,x_2 + x_1\,x_3 + x_2\,x_3 + \dots)(x_1 + x_2 + x_3 + \dots)$$

4.5 The Schur functions

The symmetric functions

$$m_\lambda,\ e_\lambda,\ h_\lambda,\ p_\lambda \tag{4.28}$$

where $\lambda \vdash n$ each form a basis for Λ^n. A very important fifth basis is realised in terms of the Schur functions, s_λ, *or for brevity, $S-$functions* which may be variously defined.

Combinatorially they may be defined as

$$s_\lambda(x) = \sum_T x^T \tag{4.29}$$

where the summation is over all semistandard $\lambda-$tableaux T. For example, consider the $S-$functions s_λ in just three variables $(x_1,\, x_2,\, x_3)$. For $\lambda = (2\,1)$ we have the eight tableaux T found earlier

$$\begin{array}{|c|c|}\hline 1&1\\\hline 2&\multicolumn{1}{|c}{}\\\cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 1&1\\\hline 3&\multicolumn{1}{|c}{}\\\cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 1&2\\\hline 2&\multicolumn{1}{|c}{}\\\cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 1&2\\\hline 3&\multicolumn{1}{|c}{}\\\cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 1&3\\\hline 2&\multicolumn{1}{|c}{}\\\cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 1&3\\\hline 3&\multicolumn{1}{|c}{}\\\cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 2&2\\\hline 3&\multicolumn{1}{|c}{}\\\cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 2&3\\\hline 3&\multicolumn{1}{|c}{}\\\cline{1-1}\end{array} \tag{3.8}$$

Each tableaux T corresponds to a monomial x^T to give

$$s_{2\,1}(x_1,\, x_2,\, x_3) = x_1^2\, x_2 + x_1^2\, x^3 + x_1\, x_2^2 + x_1\, x_2\, x_3 + x_1\, x_2\, x_3 + x_1\, x_3^2 + x_2^2\, x_3 + x_2\, x_3^2 \tag{4.30}$$

We note that the monomials in Eq.(4.30) can be expressed in terms of just two *symmetric monomials* in the three variables $(x_1,\, x_2,\, x_3)$ to give

$$s_{2\,1}(x_1,\, x_2,\, x_3) = m_{2\,1}(x_1,\, x_2,\, x_3) + 2m_{1^3}(x_1,\, x_2,\, x_3) \tag{4.31}$$

In an arbitrary number of variables

$$s_{2\,1}(x) = m_{2\,1}(x) + 2m_{1^3}(x) \tag{4.32}$$

This is an example of the general result that the $S-$function may be expressed as a linear combination of symmetric monomials as indeed would be expected if the $S-$functions are a basis of Λ^n. In fact

$$s_\lambda(x) = \sum_{\mu \vdash n} K_{\lambda\mu} m_\mu \tag{4.33}$$

where $|\lambda| = n$ and $K_{\lambda\lambda} = 1$. The $K_{\lambda\mu}$ are the elements of an upper triangular matrix K known as the Kostka matrix. K is an example of a *transition matrix* that relates one symmetric function basis to another.

4.6 Calculation of the elements of the Kostka matrix

The elements $K_{\lambda\mu}$ of the Kostka matrix may be readily calculated by the following algorithm :

i. Draw the frame F^λ.
ii. Form all possible semistandard tableaux that arise in numbering F^λ with μ_1 ones, μ_2 twos etc.
iii. $K_{\lambda\mu}$ is the number of semistandard tableaux so formed.

Thus calculating $K_{(42)\,(2^2\,1^2)}$ we obtain the four semistandard tableaux

$$\begin{array}{|c|c|c|c|}\hline 1&1&2&2\\ \hline 3&4\\ \cline{1-2}\end{array}\quad \begin{array}{|c|c|c|c|}\hline 1&1&2&3\\ \hline 2&4\\ \cline{1-2}\end{array}\quad \begin{array}{|c|c|c|c|}\hline 1&1&2&4\\ \hline 2&3\\ \cline{1-2}\end{array}\quad \begin{array}{|c|c|c|c|}\hline 1&1&3&4\\ \hline 2&2\\ \cline{1-2}\end{array}$$

and hence $K_{(42)\,(2^2\,1^2)} = 4$.

Exercises

4.5 Construct the Kostka matrix for $\lambda, \mu \vdash 4$.

4.6 Show that in the variables $(x_1,\, x_2,\, x_3)$ the evaluation of the determinantal ratio

$$\frac{\begin{vmatrix} x_1^4 & x_1^2 & 1 \\ x_2^4 & x_2^2 & 1 \\ x_3^4 & x_3^2 & 1 \end{vmatrix}}{\begin{vmatrix} x_1^2 & x_1 & 1 \\ x_2^2 & x_2 & 1 \\ x_3^2 & x_3 & 1 \end{vmatrix}}$$

yields the monomial content of the $S-$function s_{21} in three variables as found in Eq.(4.30). N.B. The above exercise is tedious by hand but trivial using MAPLEV.

The last exercise is an example of the classical definition, as opposed to the equivalent combinatorial definition given in Eq.(4.29), given first by Jacobi, namely,

$$s_\lambda = s_\lambda(x_1,\, x_2,\, \ldots, x_n) = \frac{a_{\lambda+\delta}}{a_\delta} \tag{4.34}$$

where λ is a partition of length $\leq n$ and $\delta = (n-1,\, n-2,\, \ldots,\, 1,\, 0)$ with

$$a_{\lambda+\delta} = det(x_i^{\lambda_j+n-j})_{1\leq i,j\leq n} \tag{4.35}$$

and

$$a_\delta = \prod_{1\leq i,j\leq n} (x_i - x_j) = det(x_i^{n-j}) \tag{4.36}$$

is the *Vandermonde determinant.*

4.7 Non-standard $S-$functions

The $S-$functions are symmetric functions indexed by ordered partitions λ. We shall frequently write $S-$functions $s_\lambda(x)$ as $\{\lambda\}(x)$ or, since we will generally consider the number of variables to be unrestricted, just $\{\lambda\}$. As a matter of notation the partitions will normally be written without spacing or commas separating the parts where $\lambda_i \leq 9$. A space will be left after any part $\lambda_i \geq 10$. Thus we write $\{12,11,9,8,3,2,1\} \equiv \{12\quad 11\quad 98321\}$ While we have defined the $S-$function in terms of ordered partitions we sometimes encounter $S-$functions that are not in the standard form and must convert such *non-standard* $S-$functions into standard $S-$functions. Inspection of the determinantal forms of the $S-$function leads to the establishment of the following *modification rules* :

$$\{\lambda_1, \lambda_2, \ldots, -\lambda_\ell\} = 0 \tag{4.37}$$

$$\{\lambda_1, \ldots, \lambda_i, \lambda_{i+1}, \ldots, \lambda_\ell\} = -\{\lambda_1, \ldots, \lambda_{i+1} - 1, \lambda_i + 1, \ldots, \lambda_\ell\} \tag{4.38}$$

$$\{\lambda\} = 0 \qquad \text{if } \lambda_{i+1} = \lambda_i + 1 \tag{4.39}$$

Repeated application of the above three rules will reduce any non-standard $S-$function to either zero or to a signed standard $S-$function. In the process of using the above rules trailing zero parts are omitted*.

Exercise

4.7 Show that

$$\{24\} = -\{3^2\}, \quad \{141\} = -\{321\}, \quad \{14-25-14\} = -\{3^3 2\}$$

and

$$\{3042\} = 0, \quad \{3043\} = \{3^2 2\}$$

4.8 Skew $S-$functions

The combinatorial definition given for $S-$functions in Eq.(4.29) is equally valid for skew tableaux and can hence be used to define *skew* $S-$functions $s_{\lambda/\mu}(x)$ or $\{\lambda/\mu\}$. Since the $s_{\lambda/\mu}(x)$ are symmetric functions they must be expressible in terms of $S-$functions $s_\nu(x)$ such that

$$s_{\lambda/\mu} = \sum_\nu c^\lambda_{\mu\nu} s_\nu \tag{4.40}$$

It may be shown that the coefficients $c^\lambda_{\mu\nu}$ are necessarily non-negative integers and symmetric with respect to μ and ν. The coefficients $c^\lambda_{\mu\nu}$ are commonly referred to as *Littlewood-Richardson* coefficients.

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*See also: R.C.King, B.G.Wybourne and M. Yang, *Slinkies and the $S-$function content of certain generating functions*, J.Phys.A:Math.Gen. **22**, 4519-35 (1989).

4.9 The Littlewood-Richardson rule

The product of two $S-$functions can be written as a sum of $S-$functions, viz.

$$s_\mu.s_\nu = \sum_\lambda c^\lambda_{\mu\nu} s_\lambda \tag{4.41}$$

The Littlewood-Richardson coefficients $c^\lambda_{\mu\nu}$ in Eqs. (4.40) and (4.41) are identical, though the summations are of course different. In both cases $|\mu| + |\nu| = |\lambda|$. A rule for evaluating the coefficients $c^\lambda_{\mu\nu}$ was given by Littlewood and Richardson in 1934 and has played a major role in all subsequent developments. The rule may be stated in various ways. We shall state it first in terms of semistandard tableaux and then also give the rule for evaluating the product given in Eq.(4.41) which is commonly referred to as the *outer multiplication* of $S-$functions. In each statement the concepts of a *row-word* and of a *lattice permutation* is used.

Definition 4.1 A word

Let T be a tableau. From T we derive a row-word or sequence $w(T)$ by reading the symbols in T from right to left (i.e. as in Arabic or Hebrew) in successive rows starting at the top row and proceeding to the bottom row

Thus for the tableau

$$\begin{array}{ccccc} 1 & 1 & 2 & 2 & 3 \\ 2 & 2 & 3 & 3 & \\ 4 & 4 & & & \\ 5 & 6 & & & \\ 7 & & & & \\ 8 & & & & \end{array}$$

we have the word $w(T) = 322113322446578$ and for the skew tableau

$$\begin{array}{ccccc} & & 1 & 1 & 1 \\ & 1 & 2 & 2 & \\ 1 & 2 & & & \end{array}$$

we have the word $w(T) = 11122121$.

Definition 4.2 A lattice permutation

A word $w = a_1a_2\dots a_N$ in the symbols $1, 2, \dots, n$ is said to be a lattice permutation if for $1 \le r \le N$ and $1 \le i \le n-1$, the number of occurrences of the symbol i in $a_1a_2\dots a_r$ is not less than the number of occurrences of $i+1$.

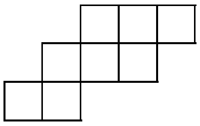
Thus the word $w(T) = 322113322446578$ is clearly not a lattice permutation whereas the word $w(T) = 11122121$ is a lattice permutation. The word $w(T) = 12122111$ is not a lattice permutation since the sub-word 12122 has more twos than ones.

Theorem 4.1 *The value of the coefficient $c^{\lambda}_{\mu\nu}$ is equal to the number of semistandard tableaux T of shape $F^{\lambda/\mu}$ and content ν such that $w(T)$ is a lattice permutation.*

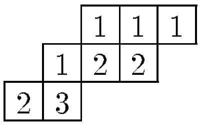
By *content* ν we mean that each tableau T contains ν_1 ones, ν_2 twos, etc.

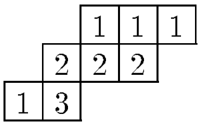
Example

Let us evaluate the coefficient $c^{\{542\}}_{\{431\}\{21\}}$. We first draw the frame $F^{\{542/21\}}$.

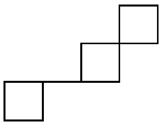


Into this frame we must inject the content of $\{431\}$ i.e. 4 ones, 3 twos and 1 three in such a way that we have a lattice permutation. We find two such numberings

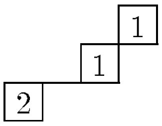


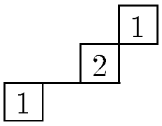


and hence $c^{\{542\}}_{\{431\}\{21\}} = 2$. Note that in the evaluation we had a choice, we could have, and indeed more simply, evaluated $c^{\{542\}}_{\{21\}\{431\}}$. In that case we would have drawn the frame $F^{\{542/431\}}$ to get



Note that in this case the three boxes are disjoint. This skew frame is to be numbered with two ones and one 2 leading to the two tableaux





verifying the previous result. Theorem 4.1 gives a direct method for evaluating the Littlewood-Richardson coefficients. These coefficients can be used to evaluate both skews and products. It is sometimes useful to state a procedure for directly evaluating products.

Theorem 4.2 *to evaluate the $S-$function product $\{\mu\}.\{\nu\}$*

1. *Draw the frame F^{μ} and place ν_1 ones in the first row, ν_2 twos in the second row etc until the frame is filled with integers.*
2. *Draw the frame F^{ν} and inject positive integers to form a semistandard tableau such that the word formed by reading from right to left starting at the top row of the first*

frame and moving downwards along successive rows to the bottom row and then continuing through the second frame is a lattice permutation.

3. Repeat the above process until no further words can be constructed.

4. Each word corresponds to an $S-$function $\{\lambda\}$ where λ_1 is the number of ones, λ_2 the number of twos etc.

As an example consider the $S-$function product $\{21\}.\{21\}$. Step 1 gives the tableau

$$\begin{array}{|c|c|}\hline 1&1\\ \hline 2 \\ \cline{1-1}\end{array}$$

Steps 2 and 3 lead to the eight numbered frames

$$\begin{array}{|c|c|}\hline 1&1\\ \hline 2 \\ \cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 1&1\\ \hline 3 \\ \cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 1&2\\ \hline 2 \\ \cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 1&2\\ \hline 3 \\ \cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 1&3\\ \hline 2 \\ \cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 1&3\\ \hline 4 \\ \cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 2&3\\ \hline 3 \\ \cline{1-1}\end{array}\quad \begin{array}{|c|c|}\hline 2&3\\ \hline 4 \\ \cline{1-1}\end{array}$$

Step 4 then lead to the eight words

$$112112 \quad 112113 \quad 112212 \quad 112213 \quad 112312 \quad 112314 \quad 112323 \quad 112324$$

from which we conclude that

$$\{21\}.\{21\} = \{42\} + \{41^2\} + \{3^2\} + 2\{321\} + \{31^3\} + \{2^3\} + \{2^21^2\}$$

Exercises

4.8 Show that* $c^{\{75321^3\}}_{\{4321\}.\{4321\}} = 8$.

4.9 Show that

$$\begin{aligned}\{31\}.\{31\} =& \{62\} + \{61^2\} + \{53\} + 2\{521\} + \{51^3\} + \{4^2\} \\ &+ 2\{431\} + \{42^2\} + \{421^2\} + \{3^22\} + \{3^21^2\}\end{aligned}$$

4.10 Show that

$$\{321/21\} = \{3\} + 2\{21\} + \{1^3\}$$

4.10 Relationship to the unitary group

We have explored various symmetric functions indexed by partitions and defined on sets of variables. The variables can admit many interpretations. In some instances we may

*The complete evaluation of the $S-$function product $\{4321\}.\{4321\}$ leads to 206 distinct frames and a total of 930 words.

choose a set of variables * $1, q, q^2, \ldots, q^n$ or we could even use a set of matrices. The link between $S-$functions and the character theory of groups is such that, if λ is a partition with $\ell(\lambda) \leq N$ and the eigenvalues of a group element, g, of the unitary group U_N are given by $x_j = \exp(i\phi_j)$ for $j = 1, 2, \ldots, N$ then the $S-$function

$$\{\lambda\} = \{\lambda_1\lambda_2 \ldots \lambda_N\} = s_\lambda(x) = s_\lambda(\exp(i\phi_1)\exp(i\phi_2)\ldots\exp(i\phi_N))$$

is nothing other than the character of g in the irreducible representation of U_N conventionally designated by $\{\lambda\}$.

The Littlewood-Richardson rule gives the resolution of the Kronecker product $\{\mu\} \times \{\nu\}$ of U_N as

$$\{\mu\} \times \{\nu\} = \sum_{|\lambda|=|\mu|+|\nu|} c_{\{\mu\}.\{\nu\}}^{\{\lambda\}}\{\lambda\} \tag{4.42}$$

where the $c_{\{\mu\}.\{\nu\}}^{\{\lambda\}}$ are the usual Littlewood-Richardson coefficients. Equation (4.42) must be modified for partitions λ involving more than N parts. Here the *modification rule* is very simple. We simply discard all partitions involving more than N parts. We shall return to these matters later in this course when we use our results to discuss the classification of many-electron states, especially for the electronic $f-$shell.

*For a practical application see R. J. Farmer, R. C. King and B. G. Wybourne, *Spectrum-generating functions for strings and superstrings*, J. Phys. A:Math.Gen. **21** 3979–4007 (1988).

Lecture Five

Before leaving the topic of $S-$functions I would like to make a few remarks about $S-$function series and briefly indicate applications to branching rules which later will play an important role in applications to atomic shell calculations.

5.1 $S-$function series

Infinite series of $S-$functions play an important role in determining branching rules and furthermore lead to concise symbolic methods well adapted to computer implementation. Consider the infinite series

$$\begin{aligned} L &= \prod_{i=1}^{\infty}(1-x_i) \\ &= 1 - \sum x_1 + \sum x_1 x_2 - \ldots \end{aligned} \tag{5.1}$$

where the summations are over all distinct terms.
e.g.

$$\sum x_1 x_2 = x_1 x_2 + x_1 x_3 + \ldots + x_2 x_3 + x_2 x_4 + \ldots \tag{5.2}$$

Recalling Eq.(4.3) we see that Eq.(5.1) is simply a signed sum over an infinite set of elementary symmetric functions e_n with

$$e_n = m_{1^n} = s_{1^n} = \{1^n\} \tag{5.3}$$

and hence Eq.(5.1) may be written as an infinite sum of $S-$functions such that

$$\begin{aligned} L &= 1 - \{1\} + \{1^2\} - \{1^3\} + \ldots \\ &= \sum_{m=0}^{\infty} (-1)^m \{1^m\} \end{aligned} \tag{5.4}$$

We may define a further infinite series of $S-$functions by taking the inverse of Eq.(5.1) to get

$$\begin{aligned} M &= \prod_{i=1}^{\infty}(1-x_i)^{-1} \\ &= 1 + \{1\} + \{2\} + \ldots \\ &= \sum_{m=0}^{\infty} \{m\} \end{aligned} \tag{5.5}$$

Clearly

$$LM = 1 \tag{5.6}$$

a result that is by no means obvious by simply looking at the product of the two series. In practice large numbers of infinite series and their associated generating functions may be constructed. We list a few of them below:

$$\boxed{\begin{array}{lll} \mathrm{A} = \sum_\alpha (-1)^{w_\alpha}\{\alpha\} & \mathrm{B} = \sum_\beta \{\beta\} & \mathrm{C} = \sum_\gamma (-1)^{w_\gamma/2}\{\gamma\} \\ \mathrm{D} = \sum_\delta \{\delta\} & \mathrm{E} = \sum_\epsilon (-1)^{(w_\epsilon+r)/2}\{\epsilon\} & \mathrm{F} = \sum_\zeta \{\zeta\} \\ \mathrm{G} = \sum_\epsilon (-1)^{(w_\epsilon-r)/2}\{\epsilon\} & \mathrm{H} = \sum_\zeta (-1)^{w_\zeta}\{\zeta\} & \mathrm{L} = \sum_m (-1)^m\{1^m\} \\ \mathrm{M} = \sum_m \{m\} & \mathrm{P} = \sum_m (-1)^m\{m\} & \mathrm{Q} = \sum_m \{1^m\} \end{array}} \tag{5.7}$$

where (α) and (γ) are mutually conjugate partitions, which in the Frobenius notation take the form

$$(\alpha) = \begin{pmatrix} a_1 & a_2 & \dots & a_r \\ a_1+1 & a_2+1 & \dots & a_r+1 \end{pmatrix} \qquad (\gamma) = \begin{pmatrix} a_1+1 & a_2+1 & \dots & a_r+1 \\ a_1 & a_2 & \dots & a_r \end{pmatrix} \tag{5.8}$$

(δ) is a partition into *even parts* only and (β) is conjugate to (δ). (ζ) is any partition and (ϵ) is any self-conjugate partition. r is the Frobenius rank of (α), (γ) and (ϵ).
These series occur in mutually inverse pairs:

$$AB = CD = EF = GH = LM = PQ = \{0\} = 1 \tag{5.9}$$

Furthermore,

$$\begin{aligned} LA = PC = E \qquad MB = QD = F \\ MC = AQ = G \qquad LD = PB = H \end{aligned} \tag{5.10}$$

We also note the series

$$R = \{0\} - 2\sum_{a,b}(-1)^{a+b+1}\begin{pmatrix} a \\ b \end{pmatrix} \qquad S = \{0\} + 2\sum_{a,b}\begin{pmatrix} a \\ b \end{pmatrix} \tag{5.11}$$

where we have again used the Frobenius notation, and

$$\begin{aligned} V = \sum_\omega (-1)^q\{\tilde{\omega}\} \qquad W = \sum_\omega (-1)^q\{\omega\} \\ X = \sum_\omega \{\tilde{\omega}\} \qquad Y = \sum_\omega \{\omega\} \end{aligned} \tag{5.12}$$

where (ω) is a partition of an even number into at most two parts, the second of which is q, and $\tilde{\omega}$ is the conjugate of ω. We have the further relations

$$RS = VW = \{0\} = 1 \tag{5.13}$$

and

$$\begin{aligned} PM = AD = W \qquad LQ = BC = V \\ MQ = FG = S \qquad LP = HE = R \end{aligned} \tag{5.14}$$

5.2 Symbolic manipulation

The above relations lead to a method of describing many of the properties of groups via symbolic manipulation of infinite series of $S-$functions. Thus if $\{\lambda\}$ is an $S-$function then we may symbolically write, for example,

$$\{\lambda/M\} = \sum_m \{\lambda/m\} \tag{5.15}$$

We can construct quite remarkable identities such as:

$$BD = \sum_\zeta \{\zeta\} \cdot \{\zeta\} \tag{5.16}$$

or for an arbitrary $S-$function $\{\epsilon\}$

$$BD \cdot \{\epsilon\} = \sum_\zeta \{\zeta\} \cdot \{\zeta/\epsilon\} \tag{5.17}$$

Equally remarkably we can find identities such as

$$\{\sigma \cdot \tau\}/Z = \{\sigma/Z\} \cdot \{\tau/Z\} \qquad \text{for} \qquad Z = L, M, P, Q, R, S, V, W \tag{5.18a}$$

$$\{\sigma \cdot \tau\}/Z = \sum_\zeta \{\sigma/\zeta Z\} \cdot \{\tau/\zeta Z\} \qquad \text{for} \qquad Z = B, D, F, H \tag{5.18b}$$

$$\{\sigma \cdot \tau\}/Z = \sum_\zeta (-1)^{w_\zeta} \{\sigma/\zeta Z\} \cdot \{\tau/\tilde{\zeta} Z\} \qquad \text{for} \qquad Z = A, C, E, G \tag{5.18c}$$

These various identities can lead to a symbolic method of treating properties of groups particulary amenable to computer implementation.

5.3 The $U_n \to U_{n-1}$ branching rule

As an illustration of the preceding remarks we apply the properties of $S-$functions to the determination of the $U_n \to U_{n-1}$ branching rules. The vector irrep $\{1\}$ of U_n can be taken as decomposing under $U_n \to U_{n-1}$ as

$$\{1\} \to \{1\} + \{0\} \tag{5.19}$$

that is into a vector $\{1\}$ and scalar $\{0\}$ of U_{n-1}. In general, the spaces corresponding to tensors for which a particular number of indices, say m, take on the value n, define invariant subspaces. Such indices must be mutually symmetrised. The irreducible representations specified by the quotient $\{\lambda/m\}$ are those corresponding to tensors obtained by contracting the indices of the tensor corresponding to $\{\lambda\}$ with an $m-$th rank symmetric tensor. Thus we may symbolically write the general branching rule as simply

$$\{\lambda\} \rightarrow \{\lambda/M\} \tag{5.20}$$

Thus for example under $U_3 \rightarrow U_2$ we have

$$\begin{aligned}\{21\} &\rightarrow \{21/M\} \\ &\rightarrow \{21/0\} + \{21/1\} + \{21/2\} \\ &\rightarrow \{21\} + \{2\} + \{11\} + \{1\}\end{aligned} \tag{5.21}$$

5.4 The Gel'fand states and the betweenness condition

The so-called Gel'fand states play an important role in the Unitary Group Approach (UGA) to many-electron theory. This comes about from considering the canonical chain of groups

$$U_n \supset U_{n-1} \supset \ldots U_2 \supset U_1 \tag{5.22}$$

The states of such a chain follow directly from consideration of Eq.(5.20). Each state may be represented by a triangular array having n rows. There are n entries $m_{i,n}$ with $i = 1, 2, \ldots, n$ corresponding to the usual partition (λ) padded out with zeroes to fill the row if need be. The second row contains $n-1$ entries $m_{i,n-1}$ placed below the first row so that the entry $m_{1,n-1}$ occurs between the entries $m_{1,n}$ and $m_{2,n}$ etc. Each successive row contains one less entry with the bottom row containing just one entry $m_{1,1}$. The number of such states is just the dimension of the irrep $\{\lambda\}$ of U_n.
Consider the irrep of U_3 labelled as $\{21\}$. We find the eight Gel'fand states

$$\begin{pmatrix} 2 & & 1 & & 0 \\ & 2 & & 1 & \\ & & 2 & & \end{pmatrix} \quad \begin{pmatrix} 2 & & 1 & & 0 \\ & 2 & & 1 & \\ & & 1 & & \end{pmatrix} \quad \begin{pmatrix} 2 & & 1 & & 0 \\ & 2 & & 0 & \\ & & 2 & & \end{pmatrix} \quad \begin{pmatrix} 2 & & 1 & & 0 \\ & 2 & & 0 & \\ & & 1 & & \end{pmatrix}$$

$$\begin{pmatrix} 2 & & 1 & & 0 \\ & 2 & & 0 & \\ & & 0 & & \end{pmatrix} \quad \begin{pmatrix} 2 & & 1 & & 0 \\ & 1 & & 1 & \\ & & 1 & & \end{pmatrix} \quad \begin{pmatrix} 2 & & 1 & & 0 \\ & 1 & & 0 & \\ & & 1 & & \end{pmatrix} \quad \begin{pmatrix} 2 & & 1 & & 0 \\ & 1 & & 0 & \\ & & 0 & & \end{pmatrix}$$

5.5 Using SCHUR to evaluate properties of $S-$functions

All of the properties of $S-$functions we have so far discussed, and many more, can be readily found using the programme SCHUR which has been placed on on the Pc's here for your experimentation.It will do many things besides just $S-$functions. e.g. Properties of irreps of all the compact Lie groups such as dimensions, Kronecker products and branching rules. However at this stage we will restrict our attention to $S-$functions. Later on in this course we will look at other features. The programme as installed has a principal file SCHUR.EXE and a large number of HELP files. Ignore all other files at this stage. Go to the SCHUR directory and enter the command SCHUR and after a few moments your screen should look like

```
SCHUR          #0333
User:Students
Site:Instytut Fizyki
Uniwersytet Mikolaja Kopernika
ul.  Grudziadzka 5/7
87-100 Torun
POLAND
Copyright.  Distribution and copying prohibited
[Version 5.0] (c) Schur Software Associates 1984,1986,1987,1988,1989
(If you wish to EXIT, enter 'END')
(If you wish to obtain HELP, enter ?'help')
DPrep Mode (with function)
DP>
-
```

Note that you can EXIT the programme any time by entering END. Also while I will indicate commands to be entered in CAPITALS the entry of commands is not case sensitive. To get to the $S-$function mode enter SFN and you will see

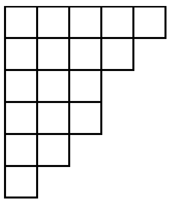
```
DP>
SFN
Schur Function Mode
SFN>
```

- You can obtain a list of commands in the Schur Function Mode by entering ?'SFNMODE' to give

```
SFN>
?'SFNMODE'
SFNmode
This mode does all calculations involving Sfns.
Commands available are:
ABsval, ADd, ALARM, ALlskew, ATtach, BELl,CDiv ,CLEave, COeffs,COLour,
CONJ, CUT, DEtach,DIGits,DIR,DISK,DIStinct, DPMode, END, EXit, FACtor,
FN,FRame, FULL, FULLSA, FSA, HALlp, Inner, INSert, LAPs, LAst, LEngth,
LIMit, LOad, LOG, LRAIse, MCount, MKWeight, MORe, MUlt, NLIMit, Outer,
```

```
PAUSE, PHase, PLeth, PLInner, POwer, QEXpand, QFN, QOUTer, QQExpand,
QQSeries, QSEries, QSKew, QSTD, RAIse, RCOnvert,REDuce, REM, REPmode,
REVerse, RInner, RQINner, RLRAIse, RRaise, SAMewt, SAve, SCONvert,
SETSfn, SKew, SQINner,STAtus,STD,STIme, SUb,SVar,TCount,TIme, TRunc,
TRWt, WEight, Zero.
Some of the Sfn commands make use  of the Sfn infinite  series (SKew,
TRunc, TRWt).
The Sfn series in Schur are:A, B, C, D, E, F, G, H, L, M, P, Q, R, S,
T, V, W, X, Y.
These series may be accessed by upper or lower case letters.
SFN>
-
```

Many of the commands you won't need to consider at the beginning. Each command has it's own helpfile. Try entering the command FRAME 54321 and you should see on your screen the frame F^{54321} drawn as



The following give examples of syntax as explained in the Helpfile DIGITS and SYNTAX. Try other frames such as 5322211 which could be entered as either FRAME532$\hat{3}$1$\hat{2}$ or as just FRAME5322211 or even as FRA5322211. To draw the frame for the partition 12 10 4321 you enter FRA !12 !10 4321 . Note that the exclamation mark (!) is put in front of digits larger than 9 and a space then follows the digits. Spaces are optional for numbers <= 9. If you enter FRA5.4321 you will see on the screen the frame F^{4321} with the digit 5 above it. To see the significance of that try entering OUTER 21,21 and you will obtain the output

```
SFN>
OUTER 21,21
{42} + {41^2 } + {3^2 } + 2{321} + {31^3 } + {2^3 } + {2^2 1^2 }
SFN>
```

- Notice that the $S-$function $\{321\}$ appears with a multiplicity of 2. Now enter FRAME LAST and you will see the frames for each partition drawn on the screen with a 2 appearing above the frame for $\{321\}$. Now try the command FRAME OUTER 21,21 and you will start to learn how you can combine sequences of commands. Enter OUTER 4321,4321 and note that you get a screen full of $S-$functions with the word MORE appearing on the left. Pressing a key will show you the next screen full. You can turn off MORE by entering MORE FALSE now repeat OUTER 4321,4321 and 206 $S-$functions

will scroll by. Try FRAME OUTER 4321,4321 and 206 frames will flash by with their associated multiplicities. To count the number of frames simply enter TCOUNT LAST and to count the sum of the multiplicities enter MCOUNT LAST.
Look at the helpfiles associated with the commands SKEW, TRWT, WEIGHT, LENGTH and see if you can determine the terms in each of the $S-$function series we have discussed today up to say weight 8. Feel free to explore the various features. See if you can make yourself a LOGFILE in which you obtain the aforementioned series and then edit the logfile and print out a neat table with suitable captions etc., possibly as a TEXfile.

Symmetry and Spectroscopic Calculations

Lecture Six

6.1 Resumé of the quantum theory of angular momentum

At the beginning of this course we introduced determinantal states. We now give an alternative description for fermions in terms of second-quantisation. The description for boson states is very similar and is left to the student to develop. Elementary courses on the quantum theory of angular momentum revolve around the structure of two important groups which are usually skillfully hidden from the student who often acquires a considerable knowledge of groups without either the teacher or student being aware of it. These two groups are the rotation group in three-dimensions SO_3 with its trivial subgroup SO_2 and the covering group of SO_3 the special unitary group in two dimensions SU_2. In the quantum theory of angular momentum we become familiar with the standard relations (throughout I take $\hbar = 1$)

$$[J_i, J_j] = i\epsilon_{ijk} J_k \tag{6.1}$$

where $i, j, k = 1, 2, 3$ and the J_i form the three components of the angular momentum $\mathbf{J}$. Putting

$$J_{\pm} = (J_1 \pm iJ_2)/\sqrt{2} \tag{6.2}$$

we can rewrite the angular momentum commutation relations as

$$[J_3, J_3] = 0, \qquad [J_3, J_{\pm}] = \pm J_{\pm}, \qquad [J_+, J_-] = J_3 \tag{6.3}$$

which are the standard commutation relations associated with the locally isomorphic Lie algebras so_3 and su_2.
We can also form an operator

$$\mathbf{J}^2 = J_1^2 + J_2^2 + J_3^2 \tag{6.4}$$

which commutes with all the components J_i and is the Casimir operator associated with the Lie algebra. As a result it is possible to construct eigenfunctions $|jm>$ that are simultaneous eigenfunctions of $\mathbf{J}^2$ and J_3 with the eigenvalue relations

$$\begin{aligned} J_3|jm> &= m|jm> \\ \mathbf{J}^2|jm> &= j(j+1)|jm> \end{aligned} \tag{6.5}$$

where

$$m = j, j-1, \ldots, -j+1, -j \tag{6.6}$$

and

$$J_{\pm}|jm> = \sqrt{j(j+1) - m(m \pm 1)}|jm \pm 1> \tag{6.7}$$

The quantum numbers m are known as *weights* with $m = j$ being the *highest* weight. We use the highest weight j to label the irreducible representations of SO_3 as $[j]$ and it follows from Eq.(6.6) that $[j]$ is of degree $(2j+1)$. If j is a non-negative integer then $[j]$ is said to be an *ordinary* or *tensor* representation whereas if j is a half-odd integer then $[j]$ is term a *spin* or *projective* representation. Both types of representations are *true* representations of SU_2.

6.2 Definition of a Lie algebra

The angular momentum operators J_i form the *infinitesimal generators* of the Lie group SO_3 and likewise the elements of the Lie algebra su_2.

Formally we define a Lie algebra as follows: Let A be an $r-$dimensional vector space over a field K in which the law of composition for vectors is such that to each pair of vectors X and Y there corresponds a vector $Z = [X, Y]$ in such a way that

$$\begin{aligned} [\alpha X + \beta Y, Z] &= \alpha[X, Z] + \beta[Y, Z] \\ [X, Y] + [Y, X] &= 0 \\ [X, [Y, Z]] + [Y, [Z, X]] + [Z, [X, Y]] &= 0 \end{aligned} \tag{6.8}$$

for all $\alpha, \beta, \ldots, \in K$ and all $X, Y, Z, \ldots, \in A$. A vector space satisfying the above relationships is said to constitute a *Lie algebra.* A given Lie algebra will be said to be *real* if K is the field of real numbers and *complex* if K is the field of complex numbers.

In many physical applications we are interested in the infinitesimal generators X_τ of a Lie group which satisfy the commutation relations

$$[X_\rho, X_\sigma] = c^\tau_{\rho\sigma} \tag{6.9}$$

with $c^\tau_{\rho\sigma} = -c^\tau_{\sigma\rho}$ and hence

$$[X_\rho, X_\rho] = 0 \tag{6.10}$$

The classification of the classical Lie algebras was essentially completed in Elié Cartan's thesis of 1894 who showed that the complex semisimple Lie algebras fall into four sequences of simple Lie algebras which he designated as A_k, B_k, C_k, and D_k where k is the *rank* of the Lie algebra. In addition Cartan found five exceptional Lie algebras which occurred for specific ranks. These were designated as G_2, F_4, E_6, E_7 and E_8. The number of group generators is equal to the dimension of the adjoint representation of the Lie algebra.

Table 6.1 The simple Lie algebras and Lie groups

Lie group	Lie algebra	Number of group generators
SU_{k+1}	A_k	$k(k+2)$
$SO_(2k+1)$	B_k	$k(2k+1)$
Sp_{2k}	C_k	$k(2k+1)$
SO_{2k}	D_k	$k(2k-1)$
G_2	G_2	14
F_4	F_4	52
E_6	E_6	78
E_7	E_7	133
E_8	E_8	248

6.3 Second quantisation

As we saw earlier we may specify a state as $|sm_s\ell m_\ell>$ in an $LS-$basis or as $|s\ell jm>$ in a $jj-$basis. Frequently we shall suppress the detailed single particle quantum numbers and just use suitable Greek letters.

It is convenient to represent angular momentum states in the language of second quantisation. For a fermionic system introduce *annihilation* or *destruction* operators a_α and *creation* operators $a_\alpha^\dagger$ such that if $|0>$ is the vacuum state then:

$$a_\alpha^\dagger|0>=|\alpha> \tag{6.11}$$

i.e. the action of the operator $a_\alpha^\dagger$ on the vacuum state $|0>$ is to create a single particle in a state specified by the set of quantum numbers α. To satisfy the antisymmetry properties of fermions we must have the *anticommutation* relations

$$\{a_\alpha, a_\beta\} = \{a_\alpha^\dagger, a_\beta^\dagger\} = 0 \tag{6.12a}$$

$$\{a_\alpha^\dagger, a_\beta\} = \delta_{\alpha,\beta} \tag{6.12b}$$

The requirement of orthonormality will be met if we take

$$a_\alpha|0>=0 \qquad \text{and} \qquad <0|a_\alpha^\dagger=0 \tag{6.13}$$

The antisymmetrisation postulate for fermions, i.e. the Pauli exclusion principle, is assured if we take

$$a_\alpha a_\alpha = a_\alpha^\dagger a_\alpha^\dagger = 0 \tag{6.14}$$

An $N-$particle state can be created by having a sequence of N fermion creation operators act on the vacuum state such that

$$a_\alpha^\dagger a_\beta^\dagger \ldots a_\omega^\dagger|0>\equiv\{\alpha,\beta,\ldots,\omega\} \tag{6.15}$$

Taking adjoints gives

$$< 0|a_\omega \dots a_\beta a_\alpha \equiv \{\alpha, \beta, \dots, \omega\}^* \tag{6.16}$$

The *number operator* is defined as

$$\sum_\zeta a_\zeta^\dagger a_\zeta \tag{6.17}$$

and acting on an arbitrary $N-$particle state $a_\alpha^\dagger a_\beta^\dagger \dots a_\omega^\dagger|0>$ gives the eigenvalue N.

6.4 One- and Two-body interactions

Single particle operators of the type

$$F = \sum_{i=1}^N f_i \tag{6.18}$$

may be expressed in second quantised form as

$$F = \sum_{\alpha,\beta} a_\alpha^\dagger < \alpha|f|\beta > a_\beta \tag{6.19}$$

while for two particle operators of the type

$$G = \sum_{1=i<j} g_{ij} \tag{6.20}$$

the second quantised form is

$$G = \frac{1}{2} \sum_{\xi,\eta,\zeta,\lambda} a_\xi^\dagger a_\eta^\dagger < \xi_1\eta_2|g_{12}|\zeta_1\lambda_2 > a_\lambda a_\zeta \tag{6.21}$$

For the angular momentum operator $\mathbf{J}$ we have

$$\mathbf{J} = \sum_{\alpha,\beta} a_\alpha^\dagger < \alpha|j|\beta > a_\beta \tag{6.22}$$

Taking $\alpha = jm$ gives the commutators

$$[J_z, a_{jm}^\dagger] = m a_{jm}^\dagger \tag{6.23a}$$

$$[J_\pm, a_{jm}^\dagger] = \sqrt{j(j+1) - m(m \pm 1)}a_{jm\pm1}^\dagger \tag{6.23b}$$

6.5 Tensor operators in general

Consider a simple compact group G having elements g. Let U_g denote a unitary, not necessarily irreducible, representation of G on a Hilbert space $\mathcal{H}$. The various unitary representations will be distinguished, when necessary, by writing $U_g(\Lambda)$ or for brevity just as (Λ). Let $|\Lambda\lambda>$ be basis vectors of the representation (Λ), where λ labels individual basis vectors.

Let the complete set of basis vectors $|\Lambda\lambda>$ span the infinite Hilbert space $\mathcal{H}$ in which the linear operator R_g (or just R) corresponding to the element g of G is represented by the block-diagonal matrix $|<\Lambda\lambda|R|\Lambda\lambda'>|$. An individual matrix element will be designated as $<\Lambda\lambda|R|\Lambda\lambda'>$. The effect of the linear operator R acting on a basis vector $|\Lambda\lambda>$ will be to produce a linear combination of those basis vectors that span the representation (Λ), that is

$$R|\Lambda\lambda>=\sum_{\lambda'}<\Lambda\lambda'|R|\Lambda\lambda>|\Lambda\lambda'> \tag{6.24}$$

The set $\mathbf{T}(\Lambda)$ of $[\Lambda]$ linearly independent operators $T(\Lambda\lambda)$ is said to form a *tensor operator* under the group G belonging to the representation (Λ) of G if under the operations of the group it transforms according to the representation (Λ) i.e., if

$$RT(\Lambda\lambda)R^{-1}=<\Lambda\lambda'|R|\Lambda\lambda>T(\Lambda\lambda') \tag{6.25}$$

A tensor operator $\mathbf{T}(\Lambda)$ will be said to be *irreducible*, *reducible* or *equivalent* if the group representation (Λ) is correspondingly irreducible, reducible or equivalent.

For an infinitesimal transformation in G

$$R=1+\delta a^{\sigma}X_{\sigma} \tag{6.26}$$

where δa^{σ} are the infinitesimal parameters and X_{σ} the corresponding infinitesimal operators. Keeping terms to first order in the δa^{σ},

$$[X_{\sigma},T(\Lambda\lambda)]=\sum_{\lambda'}<\Lambda\lambda'|X_{\sigma}|\Lambda\lambda>T(\Lambda\lambda') \tag{6.27}$$

and from Eq.(6.25)

$$X_{\sigma}|\Lambda\lambda>=\sum_{\lambda'}<\Lambda\lambda'|X_{\sigma}|\Lambda\lambda>|\Lambda\lambda'> \tag{6.28}$$

6.6 Tensor operators for SO_3

For the group SO_3 the infinitesimal operators are $J_z, J_{\pm}$ and in an angular momentum basis that diagonalises $\mathbf{J}^2$ and J_z

$$J_z|JM>=M|JM> \tag{6.29a}$$
$$J_{\pm}|JM>=\sqrt{J(J+1)-M(M\pm 1)}|JM\pm 1> \tag{6.29b}$$

which is the SO_3 equivalent of Eq.(6.25).

If $\mathbf{T}(k)$ is an irreducible tensor operator in SO_3 transforming as the irreducible representation $\mathcal{D}(k)$ of SO_3 it follows from Eq.(6.27) that the $(2k+1)$ components $T(kq)$ where $q=-k,-k+1,\ldots,k-1,k$ must satisfy the commutation relations

$$[J_z, T(kq)] = qT(kq) \tag{6.30a}$$
$$[J_\pm, T(kq)] = \sqrt{k(k+1)-q(q\pm 1)}\,T(k,q\pm 1) \tag{6.30b}$$

which we will take as the defining relations for irreducible tensor operators for SO_3. The tensor operator $\mathbf{T}(k)$ will be said to be of *rank* k.

6.7 Coupling coefficients

If $|\Lambda_1\lambda_1>$ and $|\Lambda_2\lambda_2>$ are two basis vectors of (Λ_1) and (Λ_2), respectively, then the reduction of the Kronecker product is accomplished by the *coupling coefficients*

$$<\Lambda_1\lambda_1\Lambda_2\lambda_2|\Lambda_1\Lambda_2;\alpha\Lambda_{12}\lambda_{12}>$$

where

$$|\alpha\Lambda_{12}\lambda_{12}>=\sum_{\lambda_1,\lambda_2}<\Lambda_1\lambda_1\Lambda_2\lambda_2|\Lambda_1\Lambda_2;\alpha\Lambda_{12}\lambda_{12}>|\Lambda_1\lambda_1>|\Lambda_2\lambda_2> \tag{6.31}$$

with α being a *multiplicity* symbol to distinguish repeated irreducible representations. In the case of SO_3 the coupling coefficients are just the usual Clebsch-Gordan coefficients. The inverse transformation can be written as

$$|\Lambda_1\lambda_1>|\Lambda_2\lambda_2>=\sum_{\alpha,\Lambda_{12},\lambda_{12}}<\alpha\Lambda_{12}\lambda_{12}|\lambda_1\lambda_2>^*|\Lambda_1\Lambda_2;\alpha\Lambda_{12}\lambda_{12}> \tag{6.32}$$

Since the transformations are unitary, we have the orthogonality relations

$$\sum_{\lambda_1,\lambda_2}<\alpha\Lambda_{12}\lambda_{12}|\lambda_1\lambda_2>^*<\lambda_1\lambda_2|\alpha'\Lambda'_{12}\lambda'_{12}>=\delta_{\alpha\alpha'}\delta_{\Lambda_{12}\Lambda'_{12}}\delta_{\lambda_{12}\lambda'_{12}} \tag{6.33a}$$
$$\sum_{\alpha,\Lambda_1,\Lambda_2}<\lambda_1\lambda_2|\alpha\Lambda_{12}\lambda_{12}>^*<\alpha\Lambda_{12}\lambda_{12}|\lambda'_1\lambda'_2>=\delta_{\lambda_1\lambda'_1}\delta_{\lambda_2\lambda'_2} \tag{6.33b}$$

6.8 The Wigner-Eckart theorem in general

It is the Wigner-Eckart theorem that makes group theoretical calculations quantitative. Consider a tensor operator $T(\Lambda\lambda)$ acting on a basis state $|\Lambda_2\lambda_2>$. Then

$$T(\Lambda\lambda)|\Lambda_2\lambda_2>=\sum_{\alpha,\Lambda_1,\lambda_1}<\alpha\Lambda_1\lambda_1|\Lambda\lambda\Lambda_2\lambda_2>^*|T(\Lambda)\Lambda_2;\alpha\Lambda_1\lambda_1> \tag{6.34}$$

The matrix elements of $T(\Lambda\lambda)$ are given by

$$< \Lambda_1\lambda_1|T(\Lambda\lambda)|\Lambda_2\lambda_2 >= \sum_{\alpha} < \alpha\Lambda_1\lambda_1|\Lambda\lambda\Lambda_2\lambda_2 >^* < \Lambda_1\lambda_1|T(\Lambda)|\Lambda_2; \alpha\Lambda_1\lambda_1 > \tag{6.35}$$

Consider the transformation

$$|\alpha\Lambda_1\lambda_1 >= \sum_{\beta} < \beta\Lambda_1\lambda_1|\alpha\Lambda_1\lambda_1 > |\beta\Lambda_1\lambda_1 > \tag{6.36}$$

Suppose that X_μ is an arbitrary infinitesimal operator of the group G and that

$$|\alpha\Lambda_1\lambda_1 + \mu >= \sum_{\beta} < \beta\Lambda_1\lambda_1 + \mu|\alpha\Lambda_1\lambda_1 + \mu > |\beta\Lambda_1\lambda_1 + \mu > \tag{6.37}$$

For $\mu \neq 0$

$$\begin{aligned} |\alpha\Lambda_1\lambda_1 + \mu > &= \frac{X_\mu|\alpha\Lambda_1\lambda_1 >}{< \Lambda_1\lambda_1 + \mu|X_\mu|\Lambda_1\lambda_1 >} \\ &= \sum_{\beta} < \beta\Lambda_1\lambda_1|\beta\Lambda_1\lambda_1 > |\beta\Lambda_1\lambda_1 + \mu > \end{aligned} \tag{6.38}$$

Comparison with Eq.(6.37) gives

$$< \beta\Lambda_1\lambda_1 + \mu|\alpha\Lambda_1\lambda_1 + \mu >=< \beta\Lambda_1\lambda_1|\beta\Lambda_1\lambda_1 > \tag{6.39}$$

for all $\mu \neq 0$, and hence the coefficients $< \beta\Lambda_1\lambda_1|\beta\Lambda_1\lambda_1 >$ must be independent of the component λ_1.
Making use of Eq.(6.35) gives the Wigner-Eckart theorem as

$$< \Lambda_1\lambda_1|T(\Lambda\lambda)|\Lambda_2\lambda_2 >= \sum_{\alpha} < \alpha\Lambda_1\lambda_1|\lambda\lambda_2 >^* < \alpha\Lambda_1\|T(\Lambda)\|\Lambda_2 > \tag{6.40}$$

where we have written $< \alpha\Lambda_1\|T(\Lambda)\|\Lambda_2 >$ in the place of $< \Lambda_1\lambda_1|T(\Lambda)|\Lambda_2; \alpha\Lambda_1\lambda_1 >$, since the latter is independent of λ_1. The double-barred matrix elements are independent of the weights of λ_i of the representations (Λ_i) and are referred to as *reduced matrix elements*. The entire dependence of the matrix element on the weights of the bra and ket representations together with the component of the tensor operator $\mathbf{T}(\Lambda)$ is encased in the coupling coefficients $< \alpha\Lambda_1\lambda_1|\lambda\lambda_2 >^*$. Inverting Eq.(6.40) gives

$$< \alpha\Lambda_1\|T(\Lambda)\|\Lambda_2 >= \sum_{\lambda_1,\lambda_2} < \lambda\lambda_2|\alpha\Lambda_1\lambda_1|T(\Lambda\lambda)|\Lambda_2\lambda_2 > \tag{6.41}$$

Ultimately the calculation of matrix elements comes down to the evaluation of coupling coefficients and reduced matrix elements. The Wigner-Eckart theorem may be generalised to apply successively to every group-subgroup along a chain of nested groups.

6.9 Selection rules

The Wigner-Eckart theorem leads directly to *selection rules* which follow from the requirements for the vanishing of the coupling coefficients. The coupling coefficient in Eq.(6.40) will vanish unless the weights of the bra, ket and tensor operator component satisfy the relation

$$\lambda + \lambda_2 = \lambda_1 \tag{6.42}$$

The coupling coefficient will vanish unless the triple Kronecker product

$$\Lambda_1^* \times \Lambda \times \Lambda_2 \supset 0 \tag{6.43}$$

where here 0 is the identity representation of G. We will write $c(\Lambda_1, \Lambda, \Lambda_2)$ for the number of times the identity representation occurs in the triple Kronecker product. This number gives the number of terms that occur in Eq. (6.40).

6.10 The Wigner-Eckart theorem for SO_3

The group SO_3 is *multiplicity free* and the Wigner-Eckart theorem in this case simplifies to just

$$< \alpha_1 j_1 m_1 | T_q^{(k)} | \alpha_2 j_2 m_2 >= C_{m_1 q m_2}^{j_1 k j_2} < \alpha_1 j_1 \| T^{(k)} \| \alpha_2 j_2 > \tag{6.44}$$

where $C_{m_1 q m_2}^{j_1 k j_2}$ is the usual Clebsch-Gordan coefficient. In terms of the $3j-$symbol we have

$$< \alpha_1 j_1 m_1 | T_q^{(k)} | \alpha_2 j_2 m_2 >= (-1)^{j_1 - m_1} \begin{pmatrix} j_1 & k & j_2 \\ -m_1 & q & m_2 \end{pmatrix} < \alpha_1 j_1 \| T^{(k)} \| \alpha_2 j_2 > \tag{6.45}$$

The matrix elements of $T_q^{(k)}$ vanish unless

$$m_1 = q + m_2 \tag{6.46}$$

while the reduced matrix element will vanish unless

$$j_1 + j_2 \geq k \geq |j_1 - j_2| \tag{6.47}$$

Lecture Seven

7.1 The Clebsch-Gordan coefficients

In our last lecture we introduced the Wigner-Eckart theorem for states in an angular momentum basis $|jm>$ noting that for tensor operators $\mathbf{T}^{(k)}$ we can write

$$< \alpha_1 j_1 m_1 | T_q^{(k)} | \alpha_2 j_2 m_2 >= C_{m_1 q m_2}^{j_1 k j_2} (\alpha_1 j_1 \| T^{(k)} \| \alpha_2 j_2) \tag{6.44}$$

where $C_{m_1 q m_2}^{j_1 k j_2}$ is the usual Clebsch-Gordan coefficient or in terms of the $3j-$symbol

$$< \alpha_1 j_1 m_1 | T_q^{(k)} | \alpha_2 j_2 m_2 >= (-1)^{j_1 - m_1} \begin{pmatrix} j_1 & k & j_2 \\ -m_1 & q & m_2 \end{pmatrix} < \alpha_1 j_1 \| T^{(k)} \| \alpha_2 j_2 > \tag{6.45}$$

The Clebsch-Gordan coefficient $< j_1 m_1 j_2 m_2 | j_1 j_2 j m >$ represents the elements of a unitary transformation that couples the uncoupled states $|j_1 m_1 > |j_2 m_2 >$ to produce the coupled states $|j_1 j_2 j m >$. i.e.,

$$|j_1 j_2 j m >= \sum_{m_1, m_2} < j_1 m_1 j_2 m_2 | j_1 j_2 j m > |j_1 m_1 > |j_2 m_2 > \tag{7.1}$$

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

$$|SLJM >= \sum_{M_S, M_L} < M_S M_L | SLJM > |SM_S LM_L > \tag{7.2}$$

Note that we shall often abbreviate the Clebsch-Gordan coefficient $< j_1 m_1 j_2 m_2 | j_1 j_2 j m >$ to just $< m_1 m_2 | j_1 j_2 j m >$. The Clebsch-Gordan coefficients may be expressed precisely as

$$\begin{aligned} &< m_1 m_2 | j_1 j_2 j m >= \delta_{m_1 + m_2, m} \\ &\times \sqrt{\frac{(2j+1)(j_1 + j_2 - j)!\,(j_1 - m_1)!\,(j_2 - m_2)!\,(j+m)!\,(j-m)!}{(j_1 + j_2 + j + 1)!\,(j + j_1 - j_2)!\,(j - j_1 + j_2)!\,(j_1 + m_1)!\,(j_2 + m_2)!}} \\ &\times \sum_z (-1)^{j_1 - m_1 - z} \frac{(j_1 + m_1 + z)!\,(j + j_2 - m_1 - z)!}{z!\,(j - m - z)!\,(j_1 - m_1 - z)!\,(j_2 - j + m_1 + z)!} \end{aligned} \tag{7.3}$$

While Clebsch-Gordan coefficients possesses considerable symmetry a more symmetrical object was defined by Wigner and is now commonly known as the $3j-$symbol.

7.2 The $3j-$symbol

The $3j-$symbol is related to the Clebsch-Gordan coefficient by

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1 - j_2 - m_3} \frac{< m_1 m_2 | j_1 j_2 j_3 - m_3 >}{\sqrt{(2j_3 + 1)}} \tag{7.4}$$

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. i.e.,

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} \tag{7.5}$$

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. i.e.,

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} \tag{7.6}$$

A $3j-$symbol having all its m quantum numbers zero will be null 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 lead directly to the orthonormality conditions for the $3j-$symbols

$$\sum_{j_3,m_3} (2j_3+1) \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1' & m_2' & m_3 \end{pmatrix} = \delta_{m_1,m_1'}\delta_{m_2,m_2'} \tag{7.6a}$$

$$\sum_{m_1,m_2} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j_3' \\ m_1 & m_2 & m_3' \end{pmatrix} = \frac{\delta_{j_3,j_3'}\delta_{m_3,m_3'}}{\sqrt{(2j_3+1)}} \tag{7.6b}$$

7.3 Computing $3j-$symbols

The $3j-$symbols may be variously expressed starting with the result given for the Clesch-Gordan formula given in Eq. (7.3). Extensive tables exist such as those of Rotenbrg, Bivins, Metropolis and Wooten, "*The* $3-j$ *and* $6-j$ *Symbols*" Technology Press, Mass. (1959). The difficulty with implementing formulas based upon Eq.(7.3) is the summation term which often leads to large intermediate numbers that overflow. Roothan(private communication 1990) has noted that the $3j-$symbol formula can be usefully written in the form

$$\begin{aligned} \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix} &= \sqrt{\Delta(\tfrac{b+c-\alpha}{2}, \tfrac{c+a-\beta}{2}, \tfrac{a+b+\alpha+\beta}{2})\Delta(\tfrac{b+c+\alpha}{2}, \tfrac{c+a+\beta}{2}, \tfrac{a+b-\alpha-\beta}{2})} \\ \times \sum_z (-1)^{a+b+\alpha-\beta+z} & \binom{a+b-c}{z} \binom{c+a-b}{a-\alpha-z} \binom{b+c-a}{b+\beta-z} \end{aligned} \tag{7.7}$$

where

$$\Delta(abc)^{-1} = \binom{a+b+c}{b+c-a} \binom{2a}{c+a-b} (a+b+c+1) \tag{7.8}$$

The binomial coefficients in Eq. (7.7) are first computed as integers in a Pascal's triangle and then read from the table as required and thus the awkward summation may be calculated as a sum of reals which may be rounded to produce an exact integer. The Δ terms are rapidly calculated using prime number arithmetic to produce integers and the resulting symbol outputted as a squared number expressed in prime number notation with a phase factor. With 32-bit words almost the entire tables of Rotenberg *etal* may be rapidly reproduced. With a 64-bit word such as on SUN machines the entire table and much more can be generated without overflow. On packages such as MapleV the entire calculation can be carried out using the exact arithmetic routines of MapleV.

7.4 Reduced matrix elements of angular momentum operators

The angular momentum $\mathbf{J}$ is a rank 1 tensor operator $\mathbf{J}^{(1)}$ with the $z-$ component J_z corresponding to the tensor operator component $J_0^{(1)}$. Application of the Wigner-Eckart theorem as in Eq.(6.45) gives

$$< \alpha jm|J_0^{(1)}|\alpha' j' m' >= (-1)^{j-m}\begin{pmatrix} j & 1 & j' \\ -m & 0 & m' \end{pmatrix} < \alpha j\|J^{(1)}\|\alpha' j' > \tag{7.9}$$

However, from the elementary quantum theory of angular momentum we have

$$< \alpha jm|J_z|\alpha' j' m' >= \delta_{\alpha,\alpha'}\delta_{j,j'}\delta_{m,m'}m \tag{7.10}$$

The matrix element is independent of all other quantum numbers α and diagonal in the angular momentum j. Comparison of Eqs. (7.9) and (7.10) then leads to

$$\begin{aligned} < jm|J_0^{(1)}|jm > &= m \\ &= (-1)^{j-m}\begin{pmatrix} j & 1 & j \\ -m & 0 & m \end{pmatrix} < j\|J^{(1)}\|j > \end{aligned} \tag{7.11}$$

The $3j-$symbol may be explicitly evaluated to give

$$(-1)^{j-m}\begin{pmatrix} j & 1 & j \\ -m & 0 & m \end{pmatrix} = \frac{m}{\sqrt{j(j+1)(2j+1)}}$$

from which we immediately deduce the important reduced matrix element

$$< j\|J^{(1)}\|j >= \sqrt{j(j+1)(2j+1)} \tag{7.12}$$

In deriving Eq.(7.12) we have made no assumptions as to the nature of the angular momentum and our result holds equally well for spin or orbital angular momentum operators.

7.5 The $6j-$symbol

The $3j-$symbol arose in the problem of coupling two angular momentum states to produce a coupled state. In the case of coupling three angular momenta, say j_1, j_2, j_3, to produce a total angular momentum state $|jm>$ different orders of coupling the three angular momenta can be considered. Both $|(j_1j_2)j_{12}, j_3; jm>$ and $|j_1, (j_2j_3)j_{23}; jm>$ represent distinct coupling procedures. The two coupling schemes are linked by a unitary transformation such that

$$|j_1,(j_2j_3)j_{23};jm>=\sum_{j_{12}}<(j_1j_2)j_{12},j_3;jm|j_1,(j_2j_3)j_{23};jm>|(j_1j_2)j_{12},j_3;jm> \quad (7.13)$$

Acting on both sides with j_+ shows that the transformation coefficients are independent of m.
The $6j-$symbol is defined by the relation

$$\begin{aligned}&<(j_1j_2)j_{12},j_3;jm|j_1,(j_2j_3)j_{23};jm>=\\&(-1)^{j_1+j_2+j_3+j}\sqrt{(2j_{12}+1)(2j_{23}+1)}\begin{Bmatrix} j_1 & j_2 & j_{12}\\ j_3 & j & j_{23}\end{Bmatrix}\end{aligned} \quad (7.14)$$

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

$$\begin{aligned}&\begin{Bmatrix} a & b & c\\ d & e & f\end{Bmatrix}=\\&\sqrt{\Delta(abc)\Delta(aef)\Delta(dbf)\Delta(dec)}\\&\times\sum_z(-1)^z(z+1)!\\&\times[(z-a-b-c)!(z-a-e-f)!(z-d-b-f)!(z-d-e-c)!\\&\times(a+b+d+e-z)!(b+c+e+f-z)!(a+c+d+f-z)!]^{-1}\end{aligned} \quad (7.15)$$

The $6j-$symbol vanishes unless the four triangular conditions portrayed below are satisfied.

$$\begin{Bmatrix} & & \circ & & \\ & \cdot^{\cdot^{\cdot}} & & \ddots & \\ \circ & & & & \circ\end{Bmatrix}\begin{Bmatrix}\circ & \cdots & \circ & \cdots & \circ\\ & & & & \\ & & & & \end{Bmatrix}$$
$$\begin{Bmatrix} & & & & \circ\\ & & & \cdot^{\cdot^{\cdot}} & \\ \circ & \cdots & \circ & & \end{Bmatrix}\begin{Bmatrix}\circ & & & & \\ & \ddots & & & \\ & & \circ & \cdots & \circ\end{Bmatrix} \quad (7.16)$$

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

$$\begin{aligned}&\sum_{j_{12}}(2j_{12}+1)(2j_{23}+1)\begin{Bmatrix} j_3 & j & j_{12}\\ j_1 & j_2 & j_{23}\end{Bmatrix}\begin{Bmatrix} j_3 & j & j_{12}\\ j_1 & j_2 & j'_{23}\end{Bmatrix}\\&=\delta_{j_{23},j'_{23}}\end{aligned} \quad (7.17)$$

Roothan(private communication 1990) has given the computationally convenient form for calculating $6j-$symbols

$$\begin{Bmatrix} a & b & c \\ d & e & f \end{Bmatrix}$$
$$= \sqrt{\Delta(abc)\Delta(dbf)\Delta(dec)\Delta(aef)}$$
$$\times \sum_z (-1)^z \begin{pmatrix} z+1 \\ z-a-b-c \end{pmatrix} \begin{pmatrix} b+c-a \\ z-a-e-f \end{pmatrix} \begin{pmatrix} c+a-b \\ z-d-b-f \end{pmatrix} \begin{pmatrix} a+b-a \\ z-d-e-c \end{pmatrix} \tag{7.18}$$

7.6 The $9j-$symbol

The $6j-$symbol arose in discussing the coupling of three angular momentum. Clearly more complex $nj-$symbols will arise for couplings involving more than three angular momentum. The $9j-$symbol may be defined as

$$\begin{aligned} &< (j_1j_2)j_{12},(j_3j_4)j_{34};j|(j_1j_3)j_{13},(j_2j_4)j_{24};j > \\ &= \sqrt{(2j_{12}+1)(2j_{34}+1)(2j_{13}+1)(2j_{24}+1)} \begin{Bmatrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{Bmatrix} \end{aligned} \tag{7.19}$$

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

$$\begin{aligned} &\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & i \end{Bmatrix} \\ &= \sum_z (-1)^{2z} \begin{Bmatrix} a & d & g \\ h & i & z \end{Bmatrix} \begin{Bmatrix} b & e & h \\ d & z & f \end{Bmatrix} \begin{Bmatrix} c & f & i \\ z & a & b \end{Bmatrix} \end{aligned} \tag{7.20}$$

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 arguments. If one argument of the $9j-$symbol is zero the symbol collapses to a single $6j-$symbol *viz.*

$$\begin{Bmatrix} a & b & c \\ d & e & f \\ g & h & 0 \end{Bmatrix} = \delta_{c,f}\delta_{g,h} \frac{(-1)^{b+d+f+g}}{\sqrt{(2c+1)(2g+1)}} \begin{Bmatrix} a & b & c \\ e & d & g \end{Bmatrix} \tag{7.21}$$

7.7 Coupled tensor operators

We have noted the close connection between the transformation properties of tensor operators and angular momentum states. Consider two tensor operators $\mathbf{T}^{(k_1}$ and $\mathbf{U}^{(k_2}$. We can define a coupled tensor operator $\mathbf{X}^{(k_1k_2;K)}$ via

$$\mathbf{X}_Q^{k_1k_2;K} = \sum_{q_1,q_2} T_{q_1}^{(k_1)} U_{q_2}^{(k_2)} < k_1q_1k_2q_2|k_1k_2;KQ > \tag{7.22}$$

Explicit evaluation of the Clebsch-Gordan coefficient for the case of $K = 0$ leads to

$$[\mathbf{T}^{(k)}\mathbf{U}^{(k)}]^0_0 = \frac{(-1)^k}{\sqrt{(2k+1)}} \sum_q (-1)^{-q} T^{(k)}_q U^{(k)}_{-q} \tag{7.23}$$

The scalar product of two tensor operators is defined as

$$(\mathbf{T}^{(k)} \cdot \mathbf{U}^{(k)}) = \sum_q (-1)^q T^{(k)}_q U^{(k)}_{-q} \tag{7.24}$$

It follows from Eqs.(7.22) and (7.24) that

$$[\mathbf{T}^{(k)}\mathbf{U}^{(k)}]^0_0 = \frac{(-1)^k}{\sqrt{(2k+1)}} (\mathbf{T}^{(k)} \cdot \mathbf{U}^{(k)}) \tag{7.25}$$

7.8 Matrix elements of tensor operators

Henceforth we shall often write simply $\mathbf{X}^{(K)}$ rather than $\mathbf{X}^{(k_1 k_2;K)}$ for a coupled tensor operator. It follows immediatedly from the Wigner-Eckart theorem that

$$\begin{aligned} &< \alpha j_1 j_2 J M | X^{(K)}_Q | \alpha' j'_1 j'_2 J' M' > \\ &= (-1)^{J-M} \begin{pmatrix} J & K & J' \\ -M & Q & M \end{pmatrix} < \alpha j_1 j_2 J \| X^{(K)} \| \alpha' j'_1 j'_2 J' > \end{aligned} \tag{7.26}$$

Our problem is now to evaluate the reduced matrix element in Eq.(7.26). Basically this is done by an uncoupling of the bra and ket states and of the tensor operator followed by appropriate recouplings and summations. For the details I refer you to the books of Judd and of Edmonds.

If $\mathbf{T}^{(k)}$ and $\mathbf{U}^{(k)}$ act separately on parts 1 and 2 of a system such as in spin and orbit spaces or on different particles, or sets of particles, then we obtain the result

$$\begin{aligned} < \alpha j_1 j_2 J \| X^{(K)} \| \alpha' j'_1 j'_2 J' > &= \sum_{\alpha''} < \alpha j_1 \| T^{(k_1)} \| \alpha'' j'_1 >< \alpha'' j_2 \| U^{(k_2)} \| \alpha' j'_2 > \\ &\times \sqrt{(2J+1)(2K+1)(2J'+1)} \begin{Bmatrix} j_1 & j'_1 & k_1 \\ j_2 & j'_2 & k_2 \\ J & J' & K \end{Bmatrix} \end{aligned} \tag{7.27}$$

We can specialise the above result for $K = 0$ to obtain the scalar product as

$$\begin{aligned} &< \alpha j_1 j_2 J M \| (\mathbf{T}^{(k)} \cdot \mathbf{U}^{(k)}) \| \alpha' j'_1 j'_2 J' M' > \\ &= \delta_{J,J'} \delta_{M,M'} (-1)^{j'_1 + j_2 + J} \begin{Bmatrix} j'_1 & j'_2 & J \\ j_2 & j_1 & k \end{Bmatrix} \\ &\times \sum_{\alpha''} < \alpha j_1 \| T^{(k)} \| \alpha'' j'_1 >< \alpha'' j_2 \| U^{(k)} \| \alpha' j'_2 > \end{aligned} \tag{7.28}$$

The action of an operator $\mathbf{T}^{(k)}$ acting on part 1 of a system can be found by putting $k_2 = 0$ in Eq.(7.27) to yield

$$< \alpha j_1 j_2 J \| T^{(k)} \| \alpha' j_1' j_2' J' > = \delta_{j_2, j_2'} (-1)^{j_1 + j_2 + J' + k} \sqrt{(2J+1)(2J'+1)} \left\{ \begin{array}{ccc} J & k & J' \\ j_1' & j_2 & j_1 \end{array} \right\} \times < \alpha j_1 \| T^{(k)} \| \alpha' j_1' > \tag{7.29}$$

while the action on part 2 is found by putting $k_1 = 0$ in Eq.(7.27) to yield

$$< \alpha j_1 j_2 J \| U^{(k)} \| \alpha' j_1' j_2' J' > = \delta_{j_1, j_1'} (-1)^{j_1 + j_2' + J + k} \sqrt{(2J+1)(2J'+1)} \left\{ \begin{array}{ccc} J & k & J' \\ j_2' & j_1 & j_2 \end{array} \right\} \times < \alpha j_2 \| U^{(k)} \| \alpha' j_2' > \tag{7.30}$$

A weaker result applicable to both cases where the operators act either on different parts of a system or indeed the same system may be derived to give

$$< \alpha J \| X^{(K)} \| \alpha' J' > = (-1)^{J+K+J'} \sqrt{(2K+1)} \sum_{\alpha", J"} \left\{ \begin{array}{ccc} k_2 & K & k_1 \\ J & J" & J' \end{array} \right\} \times < \alpha J \| T^{(k_1)} \| \alpha" J" > < \alpha" J" \| U^{(k_2)} \| \alpha' J' > \tag{7.31}$$

The results given by Eqs. (7.22) to (7.31) form the basis for all subsequent applications of the theory of tensor operators.

7.9 Spherical harmonics as tensor operators

The spherical harmonics $Y_{kq}(\theta, \phi)$ play a key role in many atomic and crystal field calculations. The spherical harmonics transform under the action of the generators of SO_3 just like the angular momentum states $|kq>$. Rather than using the spherical harmonics themselves it is usual to use tensor operators $\mathbf{C}^{(k)}$ whose $2k+1$ components $C_q^{(k)}$ are related to the spherical harmonics as

$$C_q^{(k)} = \sqrt{\frac{4\pi}{2k+1}} Y_{kq}(\theta, \phi) = (-1)^q \sqrt{\frac{(k-q)!}{(k+q)!}} P_k^q(\cos\theta) \exp iq\phi \tag{7.32}$$

where the $P_k^q(\cos\theta)$ are the usual Legendré polynomials.
The reduced matrix elements of $\mathbf{C}^{(k)}$ may be calculated by choosing to evaluate the matrix element of the component $C_0^{(k)}$ in an $\ell s-$basis between states with $m_\ell = 0$ as done, for example, by Judd to give

$$< \ell \| C^{(k)} \| \ell' >= (-1)^\ell \sqrt{(2\ell+1)(2\ell'+1)} \begin{pmatrix} \ell & k & \ell' \\ 0 & 0 & 0 \end{pmatrix} \tag{7.33}$$

The $3j-$symbol vanishes unless $\ell+\ell'+k$ is *even*. The corresponding result for a $jj-$basis can be found by use of Eq. (7.30) followed by Eq. (7.33) to give

$$< s\ell j\|C^{(k)}\|s\ell' j' >= (-1)^{j-\frac{1}{2}}\sqrt{(2j+1)(2j'+1)}\begin{pmatrix} j & k & j' \\ -\frac{1}{2} & 0 & \frac{1}{2} \end{pmatrix} \tag{7.34}$$

where necessarily $\ell+\ell'+k$ is *even.*

7.10 Two sum rules

In discussing transition probabilities we are often interested in summing over a set of final states to produce

$$\sum_{m_f,q} |< j_i m_i|T_q^{(k)}|j_f m_f >|^2 = \frac{1}{(2j_i+1)}|< j_i\|T^{(k)}\|j_f >|^2 \tag{7.35}$$

or sometimes over both initial and final states to produce

$$\sum_{m_i,m_f,q} |< j_i m_i|T_q^{(k)}|j_f m_f >|^2 = |< j_i\|T^{(k)}\|j_f >|^2 \tag{7.36}$$

7.11 Electric dipole transitions

The spontaneous emission transition probability per unit $\mathcal{A}$ time for an $N-$electron making transitions from an excited state $|\alpha' J' M' >$ to a lower state $|\alpha JM >$ is

$$\mathcal{A}(J'M' \to JM) = \frac{64\pi^4 e^2 a_0^2 \sigma^3}{3h}\sum_q |< \alpha JM|T_q^{(1)}|\alpha' J' M' >|^2 \tag{7.37}$$

where

$$T_q^{(1)} = \sum_{i=1}^{N} r_q^{(1)}(i) = \sum_{i=1}^{N} r_i C_q^{(1)}(i) \tag{7.38}$$

and σ is the wavenumber of the transition expressed in cm^{-1}.

The crucial quantity is the matrix element $< \alpha JM|C_q^{(1)}|\alpha' J' M' >$. Application of the Wigner-Eckart theorem gives

$$< \alpha JM|C_q^{(1)}|\alpha' J' M' >= (-1)^{J-M}\begin{pmatrix} J & 1 & J' \\ -M & q & M \end{pmatrix} < \alpha J\|C^{(k)}\|\alpha' J' > \tag{7.39}$$

The $3j-$symbol will vanish unless $(J, J', 1)$ satisfy the triangular condition and hence we have the selection rules

$$\Delta J = 0, \pm 1$$

$$0 \leftrightarrow 0 \quad \textit{forbidden}$$

Inspection of the bottom row of the $3j-$symbol requires that

$$M + q + M' = 0$$

with $q = 0, \pm 1$. This determines the polarisation properties of the radiation. If $\Delta M = 0$ the emitted light is polarised linearly and parallel to the $z-$axis. If $\Delta M = \pm 1$ we obtain circularly polarised light.
We can enlarge our description of the reduced matrix elements of $\mathbf{C}^{(1)}$ to give in an $LSJ-$basis

$$< \alpha SLJ \| C^{(1)} \| \alpha' S' L' J' > = \delta_{S,S'} (-1)^{S+L'+J+1} \sqrt{(2J+1)(2J'+1)} \left\{ \begin{array}{ccc} J & 1 & J' \\ L' & S & L \end{array} \right\} \times < \alpha L \| C^{(1)} \| \alpha' L' > \tag{7.40}$$

where we note that the tensor operator acts only on the orbital space and hence we can make use of Eq. (7.29). Inspection of the $6j-$symbol shows it will vanish unless $(L, L', 1)$ satisfy the triangular condition and hence we have the selection rules

$$\Delta S = 0, \qquad \Delta L = 0, \pm 1, \qquad L = 0 \leftrightarrow L = 0 \qquad \textit{forbidden}$$

Note these selection rules assume S and L are "*good*" quantum numbers. For a single electron orbit ℓ we can use Eq. (7.33) to evaluate the reduced matrix element in Eq. (7.40) and obtain the parity selection rule

$$\Delta \ell = \pm 1$$

a selection rule valid also for the $N-$electron case. The evaluation of the reduced matrix elements for the $N-$electron case will be considered later.

7.12 Electric dipole line strengths

The quantity

$$\mathcal{S} = | < \alpha J \| r C^{(1)} \| \alpha' J' > |^2 \tag{7.41}$$

is commonly referred to as the *electric dipole line strength.* The total transition probability from a state $|\alpha' J' M' >$ to *all* of the states $|\alpha J M >$ of the level αJ follows from application of Eq. (7.35) to give

$$\mathcal{A} = \frac{64 \pi^4 e^2 a_0^2 \sigma^3}{3h(2J'+1)} \mathcal{S} \tag{7.42}$$

In theoretical calculations the *square root* of the line strength $\mathcal{S}^{\frac{1}{2}}$ is the important quantity. We calculate the wavefunctions $|\alpha J M >$ and $|\alpha' J' M' >$ in some basis so that

$$|\alpha J M > = \sum_{\beta} a_{\alpha J}^{\beta J} |\beta J > \tag{7.43}$$

and the square root of the line strength becomes

$$\mathcal{S}^{\frac{1}{2}}(\alpha J \leftrightarrow \alpha' J') = \sum_{\beta,\beta'} a^{\beta J}_{\alpha J} < \beta J \| r C^{(1)} \| \beta' J' > a^{\beta' J'}_{\alpha' J'} \tag{7.44}$$

Such calculations of the square root of the line strength are important in taking into account departures from $LS-$coupling.

Exercises

7.1 Obtain a compact expression for the matrix element

$$< \alpha SLJM | L_z + 2S_z | \alpha SLJM >$$

7.2 Show that

$$< \alpha SLJM | L_z + 2S_z | \alpha SLJ+1M >= \sqrt{(J+1)^2 - M^2}$$
$$\times \sqrt{\frac{(S+L+J+2)(S+J+1-L)(L+J+1-S)(S+L-J)}{4(J+1)^2(2J+1)(2J+3)}}$$

In the above exercises the following special $3j-$ and $6j-$symbols are useful

$$\begin{pmatrix} j & 1 & j \\ -m & 0 & m \end{pmatrix} = (-1)^{j-m} \frac{m}{\sqrt{j(2j+1)(j+1)}}$$

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_2 & j_1 & 1 \end{Bmatrix} = (-1)^{j_1+j_2+j_3+1} \frac{(j_1(j_1+1) + j_2(j_2+1) - j_3(j_3+1)}{\sqrt{4j_1(j_1+1)(2j_1+1)j_2(j_2+1)(2j_2+1)}}$$

$$\begin{Bmatrix} j_1 & j_2 & j_3 \\ j_2-1 & j_1 & 1 \end{Bmatrix}$$
$$= (-1)^{j_1+j_2+j_3} \sqrt{\frac{2(j_1+j_2+j_3+1)(j_1+j_2-j_3)(j_2+j_3-j_1)(j_1-j_2+j_3+1)}{2j_1(2j_1+1)(2j_1+2)(2j_2-1)2j_2(2j_2+1)}}$$

Symmetry and Spectroscopic Calculations

Lecture Eight

8.1 The Zeeman effect - Weak field

Consider a magnetic field B_z directed along the $z-$axis and a set of states $|\alpha SLJM>$ associated with a spectroscopic term ^{2S+1}L. The presence of the magnetic field adds to the Hamiltonian a term

$$H_{mag} = -B_z \mu_z = B_z \mu_0 [L_z + g_s S_z] \tag{8.1}$$

where $g_s \cong 2.0023$. In terms of tensor operators we need to evaluate the matrix elements of the operator $L_0^{(1)} + g_s S_0^{(1)}$. Consider first the diagonal matrix elements

$$< \alpha SLJM | L_0^{(1)} + g_s S_0^{(1)} | \alpha SLJM >$$

Application of the Wigner-Eckart theorem, Eq.(6.45), gives

$$\begin{aligned} &< \alpha SLJM | L_0^{(1)} + g_s S_0^{(1)} | \alpha SLJM > \\ &= (-1)^{J-M} \begin{pmatrix} J & 1 & J \\ -M & 0 & M \end{pmatrix} < \alpha SLJ \| L^{(1)} + g_s S^{(1)} \| \alpha SLJ > \\ &= \frac{M}{\sqrt{J(J+1)(2J+1)}} < \alpha SLJ \| L^{(1)} + g_s S^{(1)} \| \alpha SLJ > \end{aligned} \tag{8.2}$$

Use of Eq.(7.29) gives

$$\begin{aligned} &< \alpha SLJ \| g_s S^{(1)} \| \alpha SLJ > \\ &= g_s (-1)^{S+L+J+1} (2J+1) \begin{Bmatrix} J & 1 & J \\ S & L & S \end{Bmatrix} < \alpha S \| S^{(1)} \| \alpha S > \end{aligned} \tag{8.3a}$$

Use of Eq.(7.30) gives

$$\begin{aligned} &< \alpha SLJ \| L^{(1)} \| \alpha SLJ > \\ &= (-1)^{S+L+J+1} (2J+1) \begin{Bmatrix} J & 1 & J \\ L & S & L \end{Bmatrix} < \alpha L \| L^{(1)} \| \alpha L > \end{aligned} \tag{8.3b}$$

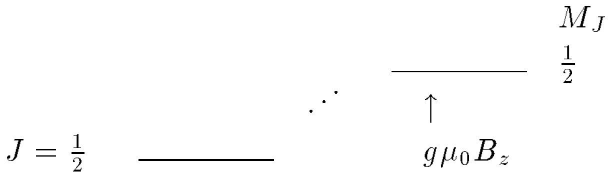
The reduced matrix elements follow from Eq.(7.12) and the $6j-$symbols may be evaluated explicitly as in Ex.(7.2). Combining terms we finally obtain

$$< \alpha SLJM | H_{mag} | \alpha SLJM >= B_z \mu_0 M g(SLJ) \tag{8.4}$$

where

$$g(SLJ) = 1 + (g_s - 1) \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \tag{8.5}$$

is the so-called Landé $g-$factor. Eq.(8.4) shows that for a weak magnetic field with states of different J well separated the magnetic field will produce splittings linearly dependent on the M quantum number. This is the so-called weak field Zeeman effect. For a $J = \frac{1}{2}$ level we obtain the pattern



$$\begin{array}{ccc} \ddots & \downarrow & \\ & \underline{\hspace{2cm}} & -\frac{1}{2} \end{array}$$

Note that we have not only determined the number of sublevels (two) but also the *magnitude* of splitting. For a $J = 1$ level we obtain the pattern

$$\begin{array}{lcccc} & & & & M_J \\ & & & \underline{\hspace{2cm}} & 1 \\ & & \iddots & \uparrow & \\ J = 1 & \underline{\hspace{2cm}} & \cdots & \underline{\hspace{2cm}} & 0 \\ & & \ddots & \downarrow & \\ & & & \underline{\hspace{2cm}} & -1 \end{array}$$

In this case we obtain three sublevels. In general we obtain $(2J + 1)$ sublevels. For a system having an *odd* number of electrons we obtain an *even* number of sublevels while for an *even* number of electrons we obtain an *odd* number of sublevels.

8.2 Off-diagonal matrix elements and the Zeeman effect

For a magnetic field in the $z-$direction the $M-$quantum number remains a good quantum number. This is because we have preserved SO_2 symmetry. However, H_{mag} does not preserve SO_3 symmetry - we have chosen a particular direction in $3-$space. The total angular momentum J is no longer a good quantum number. There exist matrix elements of H_{mag} coupling states with $\Delta J = \pm 1$. We first note that $J_z = L_z + S_z$ and hence $L_z + g_s S_z = J_z + (g_s - 1)S_z$. But the matrix elements of J_z are diagonal in J and hence to calculate the off-diagonal matrix elements we need only calculate the off-diagonal matrix element of S_z as follows:

$$\begin{aligned} &< \alpha SLJM|S_0^{(1)}|\alpha SLJ+1M > \\ &= (-1)^{J-M} \begin{pmatrix} J & 1 & J+1 \\ -M & 0 & M \end{pmatrix} < \alpha SLJ\|S^{(1)}\|\alpha SLJ+1 > \end{aligned} \tag{8.6}$$

Explicit evaluation of the $3j-$symbol gives

$$(-1)^{J-M} \begin{pmatrix} J & 1 & J+1 \\ -M & 0 & M \end{pmatrix} = -2\sqrt{\frac{(J+M+1)(J-M+1)}{(2J+1)(2J+2)}} \tag{8.7}$$

Evaluation of the reduced matrix element in Eq.(8.6) using Eq.(7.29) gives

$$\begin{aligned} &< \alpha SLJ\|S^{(1)}\|\alpha SLJ+1 > \\ &= (-1)^{S+L+J}\sqrt{(2J+1)(2J+3)} \begin{Bmatrix} J & 1 & J+1 \\ S & L & S \end{Bmatrix} < S\|S^{(1)}\|S > \\ &= -\sqrt{\frac{(S+L+J+2)(S+J+1-L)(J+1+L-S)(S-J+L)}{4(J+1)}} \end{aligned} \tag{8.8}$$

Combining Eqs. (8.7) and (8.8) in Eq.(8.6) finally yields

$$
\begin{aligned}
&< \alpha SLJM|H_{mag}|\alpha SLJ+1M > \\
&= B_z\mu_0(g_s-1)\sqrt{(J+1)^2-M^2)} \\
&\times\sqrt{\frac{(S+L+J+2)(S+J+1-L)(J+1+L-S)(S-J+L)}{4(J+1)^2(2J+1)(2J+3)}}
\end{aligned} \tag{8.9}
$$

8.3 Calculation for a ^3P term

A ^3P term has $S=1$ and $L=1$ from which we deduce that we can have $J=0,1\text{and}\quad 2$. In a free atom we expect the spin-orbit coupling to give rise to the three spectroscopic levels:

$$^3P_2 \qquad {}^3P_1 \qquad {}^3P_0$$

For simplicity we will assume $g_s=2$. From Eq.(8.5) we find

$$g(^3P_2)=\frac{3}{2} \qquad g(^3P_1)=\frac{3}{2}$$

(Recall the diagonal matrix element for a state with $M_J=0$.) The off-diagonal matrix elements follow from Eq. (8.9) and we can obtain separate matrices, one for each value of M_J. The matrices for M_J and $-M_J$ differ only in the sign of the diagonal elements which is just the sign of M_J. In units of μ_0B_z we obtain the following matrices:

$$
M_J=\pm2 \quad \begin{array}{c c} & |^3P2\pm2> \\ <^3\ P2\pm2| & \begin{pmatrix} \pm3 \end{pmatrix} \end{array} \tag{8.10a}
$$

$$
M_J=\pm1 \quad \begin{array}{c c} & \begin{array}{cc} |^3P2\pm1> & |^3P1\pm1> \end{array} \\ \begin{array}{c} <^3\ P2\pm1| \\ <^3\ P1\pm1| \end{array} & \begin{pmatrix} \pm\frac{3}{2} & \frac{1}{2} \\ \frac{1}{2} & \pm\frac{3}{2} \end{pmatrix} \end{array} \tag{8.10b}
$$

$$
M_J=0 \quad \begin{array}{c c} & \begin{array}{ccc} |^3P20> & |^3P10> & |^3P00> \end{array} \\ \begin{array}{c} <^3\ P20| \\ <^3\ P10| \\ <^3\ P00| \end{array} & \begin{pmatrix} 0 & \frac{\sqrt{3}}{3} & 0 \\ \frac{\sqrt{3}}{3} & 0 & \frac{\sqrt{6}}{3} \\ 0 & \frac{\sqrt{6}}{3} & 0 \end{pmatrix} \end{array} \tag{8.10c}
$$

The effect of the off-diagonal matrix elements is to mix states of different J and to lead to level shifts non-linear in M_J.

8.4 Strong magnetic fields and the Paschen-Back Effect

If the external magnetic field is strong and the energy separation of the different J states small then there will be strong $J-$mixing. So far we have considered states in an $|SLJM>$

basis. The calculation of energy levels requires that we add to the above matrices the other terms in the Hamiltonian such as the Coulomb and spin-orbit interactions. In the event of a very strong magnetic field we may consider states in a $|SLM_SM_L>$ basis. In that case we have the matrix elements

$$\begin{aligned}
&< \alpha SLM_SM_L|H_{mag}|\alpha SLM_SM_L > \\
&= \mu_0 B_z < \alpha SLM_SM_L|L_0^{(1)} + g_s S_0^{(1)}|\alpha SLM_SM_L > \\
&= \mu_0 B_z M_L + g_s M_S
\end{aligned} \tag{8.11}$$

where $M_J = M_S + M_L$. For the states $|^3PM_SM_L>$, taking $g_s = 2$ we have, again in units of $\mu_0 B_z$:

$$M_J = \pm 2 \quad \begin{array}{cc} & |^3P\pm1\pm1> \\ <^3P\pm1\pm1| & \begin{pmatrix} 3 \end{pmatrix} \end{array} \tag{8.12a}$$

$$M_J = \pm 1 \quad \begin{array}{cc} & \begin{array}{cc} |^3P10> & |^3P01> \end{array} \\ \begin{array}{c} <^3P10| \\ <^3P01| \end{array} & \begin{pmatrix} 2 & 0 \\ 0 & 1 \end{pmatrix} \end{array} \tag{8.12b}$$

$$M_J = 0 \quad \begin{array}{cc} & \begin{array}{ccc} |^3P1-1> & |^3P-11> & |^3P00> \end{array} \\ \begin{array}{c} <^3P1-1| \\ <^3P-11| \\ <^3P00| \end{array} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \end{array} \tag{8.12c}$$

We note, as expected these matrices are diagonal. Their eigenvalues are presiselt the eigenvalues that would be obtained if the matrices in Eq.(8.10) were diagonalised. This gives a method of checking Zeeman matrices calculated in the $|SLJM>$ basis. Upon diagonalisation we must obtain the corresponding values found in the $|SLM_SM_L>$ basis.

Exercises

(8.1). Compute the Landé $g-$values for $^2P_{\frac{1}{2}}$ and $^2P_{\frac{3}{2}}$.

(8.2). Compute the matrix element $<^2P\frac{1}{2}\frac{1}{2}|L_z + 2S_z|^2P\frac{3}{2}\frac{1}{2}>$.

(8.3). Compute the complete set of Zeeman matrices for the complete set of states associated with the ^2P multiplet in both the $|SLJM>$ and $|SLM_SM_L>$ bases.

(8.4). Use your results from the above exercises to produce a sketch showing the way the degeneracy is completely lifted by a weak magnetic field. Sketch how the sublevels behave with increasing magnetic field strength and how some degeneracies arise in the limit of a very strong magnetic field. Note in making your sketch you will want to make use of the *no crossing* theorem. In our case that means that levels of the same M_J do not cross.

(8.5). Make a list of examples from modern technology where the lifting of degeneracies by a magnetic field are exploited.

(8.6). Discuss the technological significance of departures from linearity of Zeeman splittings.

8.5 Magnetic dipole transitions

Magnetic dipole transitions are associated with the matrix elements of the magnetic dipole moment

$$\mathbf{M} = -\frac{e}{2mc}\sum_{i=1}^{n}(\mathbf{L} + \mathbf{2S})_i \tag{8.13}$$

In tensor operator form we need the matrix elements of the tensor operator

$$\mathbf{M}^{(1)} = \sum_{i=1}^{n}(\mathbf{L} + \mathbf{2S})_i^{(1)} \tag{8.14}$$

and hence the calculation of these matrix elements is exactly as for the Zeeman effect just discussed. For magnetic dipole transitions to occur they must satisfy the following selection rules:

$$\Delta\ell = 0 \quad \Delta S = 0 \quad \Delta L = 0 \quad \Delta J = 0, \pm 1 \quad J = 0 \leftrightarrow 0 \quad forbidden \tag{8.15}$$

Thus there can be no change of parity and within the approximation of $LS-$coupling transitions occur only between states of the same ${}^{(2S+1)}L$ multiplet.

Following Ofelt (*Intensities of crystal spectra of rare earth ions*, J.Chem.Phys.**37**, 511-520, 1962) it is useful to write the line strength in the form

$$\begin{aligned}&\mathcal{S}(\alpha, \beta)\\ &= (|<\alpha|M_1^{(1)}|\beta>|^2 + |<\alpha|M_{-1}^{(1)}|\beta>|^2) + |<\alpha|M_0^{(1)}|\beta>|^2\end{aligned} \tag{8.16}$$

The first term enclosed in curved brackets corresponds to π polarised light (i.e. linearly polarised parallel to the $z-$direction) and the remaining term to σ polarised light (i.e. circularly polarised). Note that this is exactly the opposite situation to electric dipole transitions and hence gives us an experimental method for distinguishing the electric dipole transitions from magnetic dipole transitions. This can be very important in crystalline materials where the *"forbidden"* magnetic dipole and *"forced"* electric dipole transitions can both occur.

Exercises

(8.7). Discuss the technological significance of magnetic dipole transitions.

(8.8). Magnetic dipole transitions are commonly referred to as *"forbidden"* transitions and are very difficult to observe in atomic spectra in the laboratory but are readily seen in the spectra of gaseous nebulae. Explain why this is the case.

(8.9). Polarisation studies show that the transitions ${}^7F_0 \Leftrightarrow {}^5D_1$ within the $4f^6$ configuration of europium salts are magnetic dipole in origin and yet such a transion appears to violate the $\Delta S = 0$ and $\Delta L = 0$ magnetic dipole selection rules. Develop a hypothesis to explain this selection rule breakdown.

(8.10). Magnetic dipole transitions, unlike electric dipole transitions, are very difficult to observe in the optical spectra of atoms but are readily seen in microwave spectra whereas electric dipole transitions are not. Explain this observation.

Lecture Nine

9.1 Spin-orbit interaction for a single electron

The spin-orbit interaction plays an important part in both atomic and nuclear physics. It arises directly out of considerations of the relativistic Dirac equation. It leads to the inclusion in the Hamiltonian of a term

$$H_{s-o} = \sum_{i=1}^{N} \zeta_{n\ell}(r_i)(\mathbf{s}\cdot\mathbf{l})_i \tag{9.1}$$

where in the central-field approximation the radial integral $\zeta_{n\ell}(r_i)$ involves just the quantum numbers $n\ell$. The radial integral $\zeta_{n\ell}$ is commonly referred to as the *spin-orbit coupling constant* and gives a measure of the strength of the spin-orbit interaction. H_{s-o} is a scalar operator and in a $|JM>$ basis its matrix elements are diagonal in J and M and are independent of M. As a consequence in writing down matrix elements we shall often suppress the M quantum number. For a single electron the relevant quantity is just $(\mathbf{s}\cdot\mathbf{l})$ whose eigenvalues may be evaluated simply by noting that $\mathbf{j} = \mathbf{l} + \mathbf{s}$ and hence

$$\mathbf{j}\cdot\mathbf{j} = \mathbf{l}\cdot\mathbf{l} + \mathbf{s}\cdot\mathbf{s} + 2\mathbf{s}\cdot\mathbf{l} \tag{9.2}$$

and hence

$$\mathbf{s}\cdot\mathbf{l} = \frac{1}{2}[j(j+1) - \ell(\ell+1) - s(s+1)] \tag{9.3}$$

But for a single electron $s = \frac{1}{2}$ and $j_\pm = \ell \pm \frac{1}{2}$ and hence we have

$$< j_+|\mathbf{s}\cdot\mathbf{l}|j_+ >= \frac{\ell}{2} \tag{9.4a}$$

and

$$< j_-|\mathbf{s}\cdot\mathbf{l}|j_- >= -\frac{(\ell+1)}{2} \tag{9.4b}$$

Thus for $\ell > 0$ a level characterised by the quantum numbers $ns\ell$ splits into two sublevels separated in energy by

$$\Delta E_{n\ell} = E_{n\ell j_+} - E_{n\ell j_-} = \frac{2\ell+1}{2}\zeta_{n\ell} \tag{9.5}$$

with the state with *lowest* j lying lowest to produce the pattern:

$$
\begin{array}{lccc}
 & & & \frac{\ell}{2}\zeta_{n\ell} \\
 & & \uparrow & \\
\ell & & \Delta E_{n\ell} & \\
 & & \downarrow & \\
 & & & -\frac{(\ell+1)}{2}\zeta_{n\ell}
\end{array}
$$

Under charge conjugation the sign of the spin-orbit interaction changes sign. This amounts to interchanging particles for holes and hence for a single hole in an otherwise filled shell (i.e. the electron configuration $n\ell^{4\ell+1}$)we simply change the sign in Eqs. (9.4a) and (9.4b) and obtain the state with $j = \ell + s$ lying lowest. Note that in nuclei the sign of the spin-orbit interaction is found to have the opposite sign to that for electrons and hence for a single nucleon the state of highest j has the lowest energy.

In triply ionised cerium, Ce^{3+}, one has the following fragment of its energy level table (in cm^{-1}) given in *Atomic Energy Levels - The Rare-Earth Elements* by Martin, Zalubus and Hagan

$5p^6 4f$	$^2F_{\frac{5}{2}}$	0
	$^2F_{\frac{7}{2}}$	2253
$5p^6 5d$	$^2D_{\frac{3}{2}}$	49737
	$^2D_{\frac{5}{2}}$	52226
$5p^6 6p$	$^2P_{\frac{1}{2}}$	122585
	$^2P_{\frac{3}{2}}$	127292

Remembering that the energy separation for a single electron due to spin-orbit interaction given in Eq. (9.5) we deduce the following empirical values for the spin-orbit coupling constants in cm^{-1}

$$\zeta_{4f} = 644 \qquad \zeta_{5d} = 996 \qquad \zeta_{6p} = 3071$$

In triply ionised ytterbium, Yb^{3+} one finds

$4f^{13}$	$^2F_{\frac{7}{2}}$	0.00
	$^2F_{\frac{5}{2}}$	10214.0

from which we deduce

$$\zeta_{4f} = 2918$$

9.2 Spin-orbit interaction in $jj-$coupling

$jj-$coupling is the natural basis for calculating spin-orbit interactions. For a state $|j^N\alpha JM>$ the interaction is completely diagonal and is simply N times that found for a single electron. We saw in earlier lectures that the states of the p^2 configuration in an $|p^2SLJM>$ basis gave rise to two terms with $J=0$ ($^1S_0$ and $^3P_0$), one term with $J=1$ ($^3P_1$) and two terms with $J=2$ ($^1D_2$ and $^3P_2$). Precisely the same $J-$values arise for the $jj-$coupled configurations $p^2_{\frac{1}{2}}$ $(J=0)$, $p^2_{\frac{3}{2}}$ $(J=0,2)$ and $p_{\frac{3}{2}}p_{\frac{1}{2}}$ $(J=1,2)$ leading to the spin-orbit matrices (in units of ζ_{np})

$$J=2 \qquad \begin{array}{c c} & \begin{array}{cc} |p^2_{\frac{3}{2}}2> & |p_{\frac{3}{2}}p_{\frac{1}{2}}2> \end{array} \\ \begin{array}{c} <p^2_{\frac{3}{2}}2| \\ <p_{\frac{3}{2}}p_{\frac{1}{2}}2| \end{array} & \begin{pmatrix} 1 & 0 \\ 0 & -\frac{1}{2} \end{pmatrix} \end{array} \tag{9.6a}$$

$$J=1 \qquad \begin{array}{c c} & |p_{\frac{3}{2}}p_{\frac{1}{2}}1> \\ <p_{\frac{3}{2}}p_{\frac{1}{2}}1| & \begin{pmatrix} 1 \end{pmatrix} \end{array} \tag{9.6b}$$

$$J=0 \qquad \begin{array}{c c} & \begin{array}{cc} |p^2_{\frac{1}{2}}0> & |p^2_{\frac{3}{2}}0> \end{array} \\ \begin{array}{c} <p^2_{\frac{1}{2}}0| \\ <p^2_{\frac{3}{2}}0| \end{array} & \begin{pmatrix} -2 & 0 \\ 0 & -1 \end{pmatrix} \end{array} \tag{9.6c}$$

9.3 Spin-orbit interaction in $n\ell^N$ configurations

The calculation of the matrix elements of the spin-orbit interaction H_{s-o} within the states $|n\ell^N\alpha SLJM>$ starts by use of Eq.(7.28) (NB in the notes of Lecture 7 replace the $\|$ by $|$ on the left-hand-side of Eq.(7.28)) to give

$$\begin{aligned} &< n\ell^N\alpha SLJ|\sum_{i=1}^{N}(\mathbf{s}\cdot\mathbf{l})_i|\alpha' S'L'J> \\ &= (-1)^{S'+L+J}\begin{Bmatrix} S' & L' & J \\ L & S & 1 \end{Bmatrix} \\ &\times\sum_{i=1}^{N}\sum_{\alpha''}<\alpha S\|s_i^{(1)}\|\alpha''S'><\alpha''L\|\ell_i^{(1)}\|\alpha'L'> \end{aligned} \tag{9.7}$$

The triangular conditions required to be satisfied for the non-vanishing of the $6j-$symbol in Eq.(9.7) lead to the selection rules for spin-orbit interaction matrix elements. These matrix elements will assuredly vanish unless

$$\Delta S=0,\pm1 \quad \Delta L=0,\pm1 \tag{9.8a}$$

or if

$$S = S' = 0 \qquad \text{or} \qquad L = L' = 0 \tag{9.8b}$$

These selection rules hold independently of the number of electrons.

The fact that the spin-orbit interaction can couple states of different spin S and/or orbital L angular momentum means that in the presence of spin-orbit interaction the quantum numbers S and L will cease to be good quantum numbers and hence we will obtain states that involve linear combinations of the basis states $|\alpha SLJM>$. As far as the spin-orbit interaction is concerned the quantum numbers JM will remain as good quantum numbers. Thus spin-orbit interaction can lead to a breakdown of the selection rules for electric-dipole, magnetic-dipole or electric-quadrupole transitions as well as departures in the Landé $g-$factors calculated for $|\alpha SLJM>$ states. These effects are often referred to as arising from *intermediate coupling* where one has neither of the extremes of $LS-$ or $jj-$coupling.

9.4 The Landé interval rule

For the particular case of the diagonal matrix elements of the spin-orbit interaction the $6j-$ symbol, and its associated phase factor, in Eq.(9.7) simplifies to (see page 71 of lecture notes)

$$\begin{aligned}&(-1)^{S+L+J}\begin{Bmatrix} S & L & J \\ L & S & 1 \end{Bmatrix} \\ &= \frac{[J(J+1)-L(L+1)-S(S+1)]}{\sqrt{4S(S+1)(2S+1)L(L+1)(2L+1)}}\end{aligned} \tag{9.9}$$

Comparison with Eq.(9.7) shows that the entire dependence of the diagonal matrix elements on the total angular momentum J is contained in the numerator of Eq.(9.9).

Consider a term ^{2S+1}L and assume that the spin-orbit interaction is weak compared with the energy separation from other terms so that off-diagonal spin-orbit matrix elements may be ignored then we may write

$$\begin{aligned}E(^{2S+1}L_J) - E(^{2S+1}L_{J-1}) &= \frac{1}{2}[J(J+1)a(SL) - J(J-1)a(SL)] \\ &= Ja(SL)\end{aligned} \tag{9.10}$$

where $a(SL)$ is independent of J and is characteristic of the particular ^{2S+1}L term and thus we may conclude that *the energy interval between two levels of a term ^{2S+1}L with consecutive values of the total angular momentum J is proportional to the larger of the two values of J* which is known as the Land'e interval rule.

9.5 Spin-orbit interaction in ℓ^2 configurations

For more than two electrons the solution of Eq.(9.7) is non-trivial requiring use of coefficients of fractional parentage. Recall that for an electron configuration ℓ^2 the terms ^{2S+1}L

all have $S+L$ *even*. To use Eq.(9.7) for ℓ^2 we need to evaluate the matrix sum

$$\sum_{i=1}^{2} < (ss)S\|s_i^{(1)}\|(ss)S' >< (\ell\ell)L\|\ell_i^{(1)}\|(\ell\ell)L' > \tag{9.11}$$

We may take for $i=1$ the tensor operators acting on part one of the system and hence use Eq.(7.29) and for $i=2$ the tensor operators acting on part two of the system and use Eq.(7.30). Remembering that both $S+L$ and $S'+L'$ are even we can combine the two terms introducing a factor of 2. The single particle reduced matrix elements $< s\|s^{(1)}\|s >$ and $< \ell\|\ell^{(1)}\|\ell >$ follow from Eq.(7.12) leading us to the final result

$$\begin{aligned} &< \ell^2 SLJ|\sum_{i=1}^{2}(\mathbf{s}\cdot\mathbf{l})_i|\ell^2 S'L'J > \\ &= -2\sqrt{s(s+1)(2s+1)\ell(\ell+1)(2\ell+1)(2S+1)(2S'+1)(2L+1)(2L'+1)} \\ &\times(-1)^{S'+L+J}\left\{\begin{matrix} S' & L' & J \\ L & S & 1\end{matrix}\right\}\left\{\begin{matrix} S & S' & 1 \\ s & s & s\end{matrix}\right\}\left\{\begin{matrix} L & L' & 1 \\ \ell & \ell & \ell\end{matrix}\right\}\end{aligned} \tag{9.12}$$

9.6 Calculation of spin-orbit matrices in p^2

For the electron configuration p^2 we have $s=\frac{1}{2}$ and $\ell=1$ and hence Eq. (9.12) becomes

$$\begin{aligned} &< p^2 SLJ|\sum_{i=1}^{2}(\mathbf{s}\cdot\mathbf{l})_i|p^2 S'L'J > \\ &= -6\sqrt{(2S+1)(2S'+1)(2L+1)(2L'+1)}(-1)^{S'+L+J} \\ &\times\left\{\begin{matrix} S' & L' & J \\ L & S & 1\end{matrix}\right\}\left\{\begin{matrix} S & S' & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2}\end{matrix}\right\}\left\{\begin{matrix} L & L' & 1 \\ 1 & 1 & 1\end{matrix}\right\}\end{aligned} \tag{9.13}$$

The values of the $6j-$symbols may be readily obtained from tables or computer to yield the spin-orbit matrices for p^2 in an $LS-$basis as

$$J=2 \qquad \begin{array}{c} \\ <^3 P_2| \\ <^1 D_2| \end{array} \begin{array}{c} \begin{array}{cc} |^3P_2> & |^1D_2> \end{array} \\ \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{2}}{2} \\ \frac{\sqrt{2}}{2} & 0 \end{pmatrix} \end{array} \tag{9.14a}$$

$$J=1 \qquad \begin{array}{c} \\ <^3 P_1| \end{array} \begin{array}{c} |^3P_1> \\ \begin{pmatrix} -\frac{1}{2} \end{pmatrix} \end{array} \tag{9.14b}$$

$$J=0 \qquad \begin{array}{c} \\ <^3 P_0| \\ <^1 S_0| \end{array} \begin{array}{c} \begin{array}{cc} |^3P_0> & |^1S_0> \end{array} \\ \begin{pmatrix} -1 & -\sqrt{2} \\ -\sqrt{2} & 0 \end{pmatrix} \end{array} \tag{9.14c}$$

9.7 Checking spin-orbit matrices

In any calculation it is highly desirable to have checking procedures. The $LS-$basis states differ from those in the $jj-$basis by a unitary transformation. This implies that for a complete set of states of the ℓ^N with a particular value of J we should have

1. The traces of the matrices in either basis should be the same.
2. The eigenvalues λ in either basis should be the same.
3. If A is a unitary matrix then $\mathcal{T}\nabla(A^p) = \sum \lambda^p$

9.8 The Hund's rule groundstate

The groundstate for the states of a configuration ℓ^N can be predicted using Hund's rules as follows:

(1). Select the terms of maximum spin multiplicity (i.e largest $(2S+1)$).

(2). From those terms select the term having the largest orbital angular momentum quantum number L.

(3). For $N \leq 2\ell+1$ select the state ${}^{2S+1}L_J$ having the *smallest* value of J while if $N > 2\ell+1$ select the *largest* value of J. By way of example, in the configuration f^3 we have the terms with $(2S+1) = 2$ and 4 so the ground term must be chosen from the quartets ${}^4SDGHI$. Of the quartets the term with largest L is ${}^4I$ which can have $J = \frac{9}{2}, \frac{11}{2}, \frac{13}{2}, \frac{15}{2}$. Thus the Hund's rule groundstate for f^3 is ${}^4I_{\frac{9}{2}}$ while for f^{11} the groundstate is ${}^4I_{\frac{15}{2}}$ as is indeed found for the groundstates of the Nd^{3+} and Er^{3+} rare earth ions respectively.

9.9 Spin-orbit interaction in the Hund's ground multiplet

Consider the configuration ℓ^N with $N \leq 2\ell+1$. Let ${}^{2S+1}L$ be the Hund's rule ground term. If $J = L+S$ and $M_J = J$ then for $M_S = S$ and $M_L = L$ we have

$$|^{2S+1}LJM >= |^{2S+1}LM_SM_L > \qquad (9.15)$$

There is a unique determinantal state associated with this special state, namely,

$$\{ \overset{+}{\ell} \ \overset{+}{\ell-1} \cdots \overset{+}{\ell-N} \} \qquad (9.16)$$

Allowing the operator $\sum_{i=1}^{N}(s_z\ell_z)_i$ to act on this determinantal state we readily find that

$$<^{2S+1} LJM|\sum_{i=1}^{N}(\mathbf{s}\cdot\mathbf{l})_i|^{2S+1}LJM >= \frac{L}{2} \qquad (9.17)$$

It follows from Eqs.(9.8) and (9.9) that

$$<^{2S+1} LJM|\sum_{i=1}^{N}(\mathbf{s}\cdot\mathbf{l})_i|^{2S+1}LJM >= [J(J+1) - L(L+1) - S(S+1)]f(SL) \qquad (9.18)$$

putting $J = L + S$ and then comparing Eqs. (9.17) and (9.18) gives for the Hund's rule multiplet

$$f(SL) = \frac{1}{4S} = \frac{1}{2N} \tag{9.19}$$

and hence we have for *any* member of the Hund's rule ground state

$$< \ell^N SLJ|\sum_{i=1}^{N}(\mathbf{s}\cdot\mathbf{l})_i|\ell^N SLJ >= \frac{1}{4S}[J(J+1) - L(L+1) - S(S+1)] \tag{9.20}$$

For $N > 2\ell + 1$ we simply take the negative of the right-hand-side of Eq.(9.20).

Exercises

(9.1). Verify that the spin-orbit matrices given in Eqs. (9.6) and (9.14) satisfy the above checks.

(9.2). Calculate the spin-orbit interaction matrices for the complete set of $jj-$coupled states associated with f^2.

(9.3). Calculate the spin-orbit matrices for the complete set of $LS-$coupled states of f^2.

(9.4). The lowest electron configurations of the neutral rare earths Nd and Dy are $4f^4 6s^2$ and $4f^{10}6s^2$, respectively. The maximal multiplicity terms of these two configurations are the ^5SDGHI terms. Atomic beam measurements for the groundstates of Nd and Er give the Landé $g-$factors of $g(Nd) = 0.60329$ and $g(Dy) = 1.24159$. Give a quantitative interpretation of these results with reasons for discrepancies between your calculated results and the experimental values.

(9.5). The ground multiplet for neutral Sm is $4f^6 6s^2(^7F)$. The energies of the seven levels of the multiplet, and their associated $g-$factors have been measured as

J	$E(^7F_J)$ cm^{-1}	$g(^7F_J)$
0	0.00	
1	292.58	1.49839
2	811.92	1.49779
3	1489.55	1.49707
4	2273.09	1.49625
5	3125.46	1.49532
6	4020.66	1.49417

Use Eq.(9.20) to deduce a value of the spin-orbit coupling constant for neutral samarium and determine to what extent the Landé interval rule is satisfied. Calculate the Landé $g-$factors for each state and compare them with the corresponding experimental values.

(9.6). Perform a similar analysis for the ground multiplet of neutral Promethium (Pm) $4f^5 6s^2(^6H)$. The energies of the six levels of the multiplet, and their associated $g-$factors have been measured as

J	$E(^6H_J)$ cm^{-1}	$g(^6H_J)$
$\frac{5}{2}$	0.00	0.305
$\frac{7}{2}$	803.82	0.8279
$\frac{9}{2}$	1748.78	1.068
$\frac{11}{2}$	2797.10	1.205
$\frac{13}{2}$	3919.03	1.307
$\frac{15}{2}$	5089.79	1.33

Exercises

1. Show that if the Slater radial integrals in the $f-$shell satisfy the special values
$$\frac{F_4}{F_2} = \frac{6}{11} \quad \text{and} \quad \frac{F_6}{F_2} = \frac{1}{11}$$
then in f^2 the Coulomb energies degenerate to
$$E(^3P) = E(^3F) = E(^3H) = F_0 - 54F_2$$
$$E(^1D) = E(^1G) = E(^1I) = F_0 + 30F_2$$
$$E(^1S) = F_0 + 324F_2$$
This is an example of the Laporte-Platt degeneracies.
2. Show that for f^2 in $jj-$coupling the two $J = 0$ states come from the $\frac{7}{2}^2$ and $\frac{5}{2}^2$ configurations.
3. Show that in $jj-$coupling for the $f-$shell
$$< \frac{7}{2}^2 J = 0|H_C|\frac{7}{2}^2 J = 0 >=$$
$$F_0 + \frac{375}{7}F_2 + \frac{891}{7}F_4 + 429F_6$$
$$< \frac{5}{2}^2 J = 0|H_C|\frac{5}{2}^2 J = 0 >=$$
$$F_0 + \frac{360}{7}F_2 + \frac{726}{7}F_4$$
$$< \frac{7}{2}^2 J = 0|H_C|\frac{5}{2}^2 J = 0 >=$$
$$\frac{2}{7\sqrt{3}}45F_2 + 495F_4 + 9009F_6$$

4. Use the values of the Slater radial integrals from 1. and diagonalise the rank 2 matrix found in 3. to show that the energies obtained are identical to those for $E(^1S)$ and $E(^3P)$ found in 1.