High Symmetry States with Examples

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A monographic series of six lectures

■ Lecture 1

■ 1. Introduction

Icosahedral symmetry was thought by physicists to be devoid of physical interest and largely ignored. Interest in icosahedral symmetry developed with the observation of approximate icosahedral symmetry in rare earth double nitrates, the discovery of icosahedral polyborane molecules and most dramatically with the discovery of the buckminster fullerenes.

In this short series of approximately six lectures I shall outline the properties of the icosahedral group $\mathcal{I}$, its relationship to the alternating group $\mathcal{A}_5$, the reduction of angular momentum states $|JM\rangle$ to icosahedral states and the subgroups of the icosahedral group. The concept of invariant operators and integrity bases will be introduced and constructive examples given in detail using MAPLE. Finally I will discuss the classification of many-electron states in high symmetry fields.

This is meant to be an introductory course and if there is interest may be later followed by a more advanced course. I shall assume familiarity with the quantum theory of angular momentum. A number of exercises using MAPLE will be given.

■ 2. Regular Polygons

A regular plane polygon has all its edges equal and all its angles equal.

Examples:- equilateral Triangle, Square, Pentagon, Hexagon, ... ,Circle.

Unless otherwise stated whenever I refer to a triangle I will imply an equilateral triangle. Only the triangle, square and hexagon, (the latter known to bees) are able to fill a plane without gaps. This simple observation lead most physicists to discard the possibility of solids possessing the five-fold symmetry associated with the regular pentagon and in particular to miss the possibility of non-periodic five-fold symmetry.

■ 3. Regular Polyhedra

The faces of a regular polyhedron are all regular polygons of the same type with all vertices equivalent. Just five regular polyhedra are possible.

Name	Shape of Faces	Number of Faces	Number of Vertices	Number of Edges
Tetrahedron	Triangle	4	4	6
Cube	Square	6	8	12
Octahedron	Triangle	8	6	12
Dodecahedron	Pentagon	12	20	30
Icosahedron	Triangle	20	12	30

■ 4. Duality

A cube may be inscribed in a regular octahedron by placing a vertex in the centre of each face of the octahedron. Likewise, a regular octahedron may be inscribed in a cube. Thus a duality exists between the cube and the octahedron. This has an important consequence for us - the symmetry groups of the cube and the octahedron are isomorphic to each other. Their group elements have the same Cayley multiplication table, the same group representations and the same group character table.

Likewise, the icosahedron and dodecahedron are dual and hence their symmetry groups are isomorphic. Throughout these lectures we will concentrate on icosahedral symmetry and remembering the duality no significant new features arise for dodecahedral symmetry.

NB. The tetrahedron stands alone among the regular polyhedrons in not having a dual partner.

■ 5. Semiregular Polyhedra

Semiregular polyhedra (also known as Archimedean Polyhedra). The faces of these polyhedra are all regular polygons but not all faces are identical. Their vertices are all alike. These polyhedra are formed by symmetrically cutting off the corners of regular polyhedra. There are thirteen semiregular polyhedra as shown below:-

■ 6. The Truncated Icosahedron, Buckyball or Soccer Ball

The truncated icosahedron has 32 faces consisting of 12 regular pentagons and 20 regular hexagons. There are 60 vertices. THe edges of the pentagons and hexagons are of equal length. The fact that the construction exists in the form of a soccer ball shows that the truncated icosahedron is a good approximation to a sphere. The unfolded truncated icosahedron is shown below:-

■ 7. The dihedral group $\mathcal{D}_3$

Consider an equilateral triangle lying in a plane. It is clearly left invariant by a clockwise rotation, C_3, through 120° about an axis perpendicular to the plane and passing through the centre of the triangle. Likewise, it is left invariant by rotation, C_3^2, through 240° or equivalently, a counterclockwise rotation, C_3^{-1}, through -120°. It follows that applying C_3 followed by C_3^{-1} returns our triangle to its original position and

$$C_3 \times C_3^{-1} = C_3^{-1} \times C_3 = \mathcal{E} \tag{1}$$

where $\mathcal{E}$ is termed the *identity operation**. Thus we have discovered three symmetry elements

$$\{\mathcal{E},\ C_3,\ C_3^{-1}\} \tag{2}$$

which form the elements of a group, the cyclic group, $\mathcal{C}_3$.

If our triangle has indistinguishable faces then we have a higher symmetry since our triangle will be left invariant under two-fold rotations, C_2, about any of the three axes lying in the plane and passing through a vertex and centre of the triangle. This larger symmetry group is the dihedral group, $\mathcal{D}_3$ with the six element set

$$\{\mathcal{E},\ C_3,\ C_3^{-1},\ 3C_2\} \tag{3}$$

■ 8. The Isomorphism $\mathcal{D}_3 \sim \mathcal{S}_3$

The dihedral group $\mathcal{D}_3$ is isomorphic with the group of permutations on three objects, the symmetric group $\mathcal{S}_3$. This may be readily established by labelling the vertices of the triangle clockwise with the integers $1, 2, 3$ and noting that each rotation can be uniquely associated with a permutation of the three integers. Indeed we have the correspondences:-

$$\begin{gathered}
\mathcal{E} \equiv \begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix}, \quad C_3 \equiv \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix}, \quad C_3^{-1} \equiv \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix} \\
C_2(12) \equiv \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix}, \quad C_2(23) \equiv \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix}, \quad C_2(13) \equiv \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix}
\end{gathered} \tag{4}$$

For convenience we shall in future use one-line notation to designate a permutation and suppress all one cycles except for the identity element, $\mathcal{E}$, writing

$$\begin{gathered}
(1)(2)(3) \equiv \begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix}, \quad (123) \equiv \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix}, \quad (132) \equiv \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix} \\
(12) \equiv \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix}, \quad (23) \equiv \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix}, \quad (13) \equiv \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix}
\end{gathered} \tag{5}$$

The elements of the group $\mathcal{S}_3$ are thus the six-element set

$$\mathcal{E},\ (123),\ (132),\ (12),\ (23),\ (13) \tag{6}$$

Note that the identity element, $\mathcal{E}$, involves three $1-$cycles, there are two elements involving $3-$cycles and two elements involving $2-$cycles. The three elements $\mathcal{E},\ (123),\ (132)$ form a subgroup of $\mathcal{S}_3$, the group of *even* permutations** on three objects, namely, The alternating group $\mathcal{A}_3$. We thus have two pairs of isomorphic groups

$$\mathcal{C}_3 \sim \mathcal{A}_3, \qquad \mathcal{D}_3 \sim \mathcal{S}_3 \tag{7}$$

This means that there is a one-to-one correspondence between the elements of the isomorphic pairs of groups. They share the same character table, Kronecker products, Cayley multiplication table etc. This also means that all the theory of the alternating and symmetric groups can be exploited.

* NB while the rotations in Eq (1) commute in general rotation do not commute. Show this by performing two successive rotations of a book and then reversing the sequence of applying the two rotations.

** In general a permutation is even if the number of even cycles is even otherwise the permutation is odd. The symmetric group $\mathcal{S}_n$ has $n!$ distinct permutations, half of these are even permutations and form the $\frac{n!}{2}$ elements of the alternating group, $\mathcal{A}_n$.

9. Further Isomorphic Sets of Finite Groups

It is not difficult to establish further isomorphic pairs of groups. In the case of the cube, $\mathcal{C}$, there are four diagonals and every operation on the cube that transforms it into itself can be represented as a permutation. Unlike the $\mathcal{D}_3$ case both *even* and *odd* permutations leave the cube invariant. Further, recalling that the octahedron and cube are dual polyhedra we have the isomorphic triplet

$$\mathcal{O} \sim \mathcal{C} \sim \mathcal{S}_4 \tag{8}$$

In the case of the tetrahedron, $\mathcal{T}$, only *even* permutations leave the tetrahedron invariant and we have the isomorphic pair of groups

$$\mathcal{T} \sim \mathcal{A}_4 \tag{9}$$

Finally, for the icosahedron, $\mathcal{I}$, and its dual, the dodecahedron $\mathcal{D}$ we can draw five diagonals and every *even* permutation leaves the polyhedron invariant and hence we have the isomorphic triplet

$$\mathcal{I} \sim \mathcal{D} \sim \mathcal{A}_5 \tag{10}$$

Again we see the alternating and symmetric groups appearing.

10 Some Important Subgroups

In many cases of high symmetry the symmetry may become *broken* by some interactions or distortion of the system leaving some subgroup as the actual symmetry group of the system. Thus it is important to know the possible subgroups of each symmetry group. In the case of the icosahedral group we have the important distinct proper subgroups

$$\mathcal{I} \supset \mathcal{T}, \quad \mathcal{D}_5, \quad \mathcal{D}_3, \quad \mathcal{C}_5, \quad \mathcal{D}_2, \quad \mathcal{C}_3, \quad \mathcal{C}_2, \quad \mathcal{C}_1 \tag{11}$$

In studying the breaking of symmetry we need to determine how degeneracies are lifted and for this we turn to the group character tables.

11 Character Tables

The character tables of the various finite groups provide the key to obtaining many of the properties of systems exhibiting high symmetry. In general the larger the symmetry group the higher are the possible degeneracies. These are simply given by the dimension of the irreducible representation matrices of the group. In this course we shall hardly consider explicit representation matrices as we shall obtain most of our information from the character tables which give the *traces* of the representation matrices. These traces are the same for all members of a given class. Let us now, for future use present some of the character tables that will be needed in our course:-

Character Table[◇] **for the Tetrahedral Group $\mathcal{T}$**

$$\begin{array}{c|cccc}
 & 1 & 3C_2 & 4C_3 & 4C_3' \\
\hline
A_1 & 1 & 1 & 1 & 1 \\
A_2 & 1 & 1 & 1 & -1 \\
E\begin{cases} \\ \\ \end{cases} & \begin{matrix} 1 \\ 1 \end{matrix} & \begin{matrix} 1 \\ 1 \end{matrix} & \begin{matrix} \omega \\ \omega^2 \end{matrix} & \begin{matrix} \omega^2 \\ \omega \end{matrix} \\
T & 3 & -1 & 0 & 0
\end{array}$$

Character Table for the Dihedral Group $\mathcal{D}_5$

$$\begin{array}{c|cccc}
 & 1 & 2C_5 & 2C_5^2 & 5C_2 \\
\hline
A_1 & 1 & 1 & 1 & 1 \\
A_2 & 1 & 1 & 1 & -1 \\
E_1 & 2 & -\frac{1}{2}(1-\sqrt{5}) & -\frac{1}{2}(1+\sqrt{5}) & 0 \\
E_2 & 2 & -\frac{1}{2}(1+\sqrt{5}) & -\frac{1}{2}(1-\sqrt{5}) & 0
\end{array}$$

◇ Here $\omega = \frac{1}{2}(-1 + i\sqrt{3})$

Character Table for the Octahedral Group $\mathcal{O}$

$$
\begin{array}{c}
\\ A_1 \\ A_2 \\ E \\ T_1 \\ T_2
\end{array}
\begin{array}{c}
\begin{array}{ccccc} 1 & 8C_3 & 3C_2 & 6C_2' & 6C_4 \end{array} \\
\begin{bmatrix}
1 & 1 & 1 & 1 & 1 \\
1 & 1 & 1 & -1 & -1 \\
2 & -1 & 2 & 0 & 0 \\
3 & 0 & -1 & -1 & 1 \\
3 & 0 & -1 & 1 & -1
\end{bmatrix}
\end{array}
$$

Character Table for the Icosahedral Group $\mathcal{I}$

$$
\begin{array}{c|ccccc}
 & 1 & 20C_3 & 15C_2 & 12C_5 & 12C_5^2 \\
\hline
A & 1 & 1 & 1 & 1 & 1 \\
T_1 & 3 & 0 & -1 & \frac{1}{2}(1+\sqrt{5}) & \frac{1}{2}(1-\sqrt{5}) \\
T_2 & 3 & 0 & -1 & \frac{1}{2}(1-\sqrt{5}) & \frac{1}{2}(1+\sqrt{5}) \\
U & 4 & 1 & 0 & -1 & -1 \\
V & 5 & -1 & 1 & 0 & 0
\end{array}
$$

The degeneracy associated with a particular irreducible representation is given by its characteristic for the identity element which is given in the first column of the relevant character table. Thus for the icosahedral group we can have degeneracies as high as 5 (for the V irreducible representation). This results, as we shall see later in the fact that a pure $d-$orbital cannot split in icosahedral symmetry. If we see a splitting then either the symmetry is broken or the $d-$orbital contains admixtures of, at least, $f-$ or $g-$orbitals.

■ 12 Inversion Symmetry

Inspection of the regular polyhedra makes it readily apparent that in addition to invariance with respect to pure rotations they possess invariance with respect to an inversion about their centre. Including inversion symmetry doubles the number of group elements but does not change the degeneracies. Rather the representations become doubled with half of them being *even* or *gerade* g and the other half being *odd* or *ungerade* u. These irreducible representations are labelled as usual except for the attachment of the appropriate g or u as a subscript. In the case of the icosahedral group, $\mathcal{I}$ we label the group, with the inclusion of inversion symmetry, as $\mathcal{I}_h$ and have the much larger set of possible subgroups

$$\mathcal{I}_h, \mathcal{I}, \mathcal{T}_h, \mathcal{T}, \mathcal{D}_{5v}, \mathcal{D}_5, \mathcal{C}_{5v}, \mathcal{C}_5, \mathcal{S}_{10}, \mathcal{D}_3, \mathcal{D}_{2h}, \mathcal{S}_6, \mathcal{C}_{3v}, \mathcal{C}_3, \mathcal{C}_{2v}, \mathcal{C}_{2h}, \mathcal{C}_2, \mathcal{S}_2, \mathcal{C}_{1h}, \mathcal{C}_1 \tag{12}$$

The existence of inversion symmetry has important spectroscopic consequences since the existence of a centre of inversion precludes pure electric-dipole transitions though not magnetic-dipole or electric-quadrupole transions. This does not, however, preclude the possibility of observing electronic-vibronic transitions.

■ 13 Note on the Symmetric Groups $\mathcal{S}_n$

The symmetric group*** $\mathcal{S}_n$ has $n!$ elements whose elements may be divided into *classes* with each class labelled by a *partition*, (λ), of the integer n. We will normally write such partitions in reverse lexicographic order, Thus for $\mathcal{S}_4$ we have the five classes

$$(1^4),\ (21^2),\ (2^2),\ (31), (4) \tag{13}$$

Repeated parts of a partition are written as exponents in the form i^{m_i} where m_i is the number of times the integer i appears in the partition. The permutations belonging to a class (λ) all have the same cycle structure, the number of cycles of length i being just m_i. Thus in $\mathcal{S}_4$ the class (21^2) contains the have one cycle of length 2 and two of length 1. The number of elements h_λ associated with a class (λ) of cycle structure $1^{m_1}2^{m_2}\ldots$ is

$$h_\lambda = \frac{n!}{\prod_{i=1} i^{m_i} m_1!} \tag{14}$$

*** For an excellent introduction to the theory of the symmetric group see:- B. E. Sagan, *The Symmetric Group*; see also:- Luan Dehuai and B. G. Wybourne, J. Phys. A: Math. Gen. **14**, 327 (1981)

Thus for $\mathcal{S}_4$ we have the class numbers, in square brackets,

$$(1^4)[1],\ (21^2)[6],\ (2^2)[3],\ (31)[8],\ (4)[6] \tag{15}$$

The irreducible representations of $\mathcal{S}_n$ may be uniquely labelled by order partitions of the integer n. For irreducible representations, as opposed to classes, we will enclose the partitions in curly brackets, thus $\{\lambda\}$. The character table for $\mathcal{S}_4$ would be written as

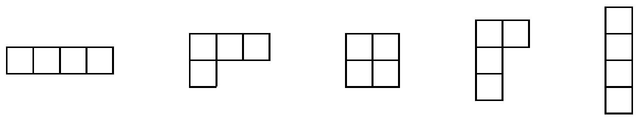
Character Table for the Symmetric Group $\mathcal{S}_4$

$$\begin{array}{c} \\ \{4\} \\ \{1^4\} \\ \{2^2\} \\ \{31\} \\ \{21^2\} \end{array} \begin{array}{c} \begin{array}{ccccc} (1^4)[1] & (31)[8] & (2^2)[3] & (21^2)[6] & (4)[6] \end{array} \\ \left[\begin{array}{ccccc} 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & -1 & -1 \\ 2 & -1 & 2 & 0 & 0 \\ 3 & 0 & -1 & -1 & 1 \\ 3 & 0 & -1 & 1 & -1 \end{array}\right] \end{array}$$

Where we have arranged the classes and irreducible representations to emphasize the isomorphism with the octahedral group $\mathcal{O}$.

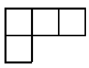
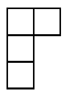
■ 14 Note on Young Frames

For any partition $(\lambda) \equiv (\lambda_1, \lambda_2, \ldots)$ we may draw a Young frame as a series of left adjusted boxes with λ_1 boxes in the first row, λ_2 boxes in the second row etc. Thus for the partitions of the integer 4 we have the five frames

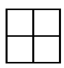


- We will formally designate the frame associated with a partition λ as F^λ.
- The *conjugate* of a partition λ is a partition λ' whose diagram is the transpose of the diagram of λ. If $\lambda' \equiv \lambda$ then the partition λ is said to be *self-conjugate*.

Thus

 and 

are conjugates while



is self-conjugate. Irreducible representations of $\mathcal{S}_n$ labelled by self-conjugate partitions are said to be *self-associated*.

A partition (λ) will be said to be *greater* than a partition (μ) if the first non-vanishing $\lambda_i - \mu_i$ is *positive*. Thus partitions of 4 in order of decreasing greatness would be

$$(4) > (31) > (2^2) > (21^2) > (1^4) \tag{16}$$

■ 14 Note on the Alternating Group $\mathcal{A}_n$

The alternating group**** $\mathcal{A}_n$, contains just those classes of the corresponding symmetric group, $\mathcal{S}_n$, involving even permutations. However there is an important difference for those classes in which the even permutations involve only *odd* cycles of *unequal* length. In those cases the class splits into two classes of conjugate elements of $\mathcal{A}_n$ each with half the number of elements. These *splitting classes* may be distinguished by attaching a $\pm$ to the class partition. Thus in $\mathcal{S}_3$ there are two permutations of cycle length 3 belonging to the class (3), namely (123), (132). In $\mathcal{A}_3$ the class (3) splits into $(3)_+$ and $(3)_-$ each containing one permutation.

The irreducible representations of $\mathcal{A}_n$ may also be labelled by partitions of n with two important differences.

**** See:- Luan Dehuai and B. G. Wybourne, J. Phys. A: Math. Gen. **14**, 1835 (1981)

1. For conjugate partitions we use only the greatest partition.
2. For self-conjugate partitions there is a splitting into two conjugate irreducible representations which we will distinguish by attaching a $\pm$ to the partition.

Thus for A_5 we have the irreducible representations

$$\{5\}(A),\ \{41\}(U),\ \{32\}(V),\ \{31^2\}_+(T_1),\ \{31^2\}_-(T_2) \tag{17}$$

where we have placed in curved brackets the corresponding labels for the isomorphic icosahedral group. The simple characters of $\mathcal{S}_n$ corresponding to irreducible representations that are not self- associated are also simple characters of $\mathcal{A}_n$ whereas for the splitting irreducible representations the characteristics are *half* those for $\mathcal{S}_n$ except for the splitting classes, the characteristics of the two classes being interchanged for the second character$^{\diamond\diamond}$.

■ 15 The Orthogonal Groups SO_n and O_n

The infinite set of unimodular orthogonal $n \times n$ matrices, of determinant $+1$, form the elements of the special orthogonal group SO_n, the case of $SO3$ being the standard group of continuous pure rotations in $3-$space. Consideration of matrices of determinant ± 1 leads to the full orthogonal group O_n which may be regarded as being SO_n augmented with discrete reflections. Thus while $SO_3 \supset \mathcal{I}$ the group $\mathcal{I}_h$ is NOT a subgroup of SO_3 but rather $O_3 \supset \mathcal{I}_h$. The groups O_3 and SO_3 are associated with spherical symmetry - the symmetry of free space. Placing an atom, ion or molecule in a solid will normally break the spherical symmetry down to that of one of the point groups, most commonly to one of the 32 crystallographic point groups$^{\diamond\diamond\diamond}$. The lowering of the symmetry from spherical will frequently involve a lowering of degeneracy. The determination of the precise degeneracy reductions follows from the branching rules for the group reduction from O_3, or SO_3, to the appropriate finite subgroup. This will be taken up in the next lecture.

High Symmetry States with Examples

B. G. Wybourne

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■ Lecture 2

■ 1. Introduction

In this lecture we shall first give a brief review of the orthogonal group SO_3 and then show how to use MAPLE to calculate characteristics of SO_3 for some angles of rotation of interest. This then leads to the establishment of the branching rules for finite subgroups of SO_3.

■ 2. A Brief Review of the Orthogonal Group SO_3

The group SO_3 is familiar to most physicists from their acquaintance with the quantum theory of angular momentum (QTA) and hence I shall only sketch some relevant details. The QTA is characterised by the commutation relations (throughout we take $\hbar = 1$)

$$[J_+, J_-] = 2J_z \qquad [J_\pm, J_z] = \pm J_z \tag{1}$$

We can form an operator, the *Casimir operator*

$$J^2 = \frac{1}{2}(J_+J_- + J_-J_+) + J_z^2 \tag{2}$$

which commutes with all the operators in Eq.(1). We can form an *angular momentum basis* that simultaneously diagonalises the operators $\{J^2, J_z\}$ and which is characterised by the eigenvalues of those operators such that

$$\begin{aligned} J^2|JM\rangle &= J(J+1)|JM\rangle \\ J_z|JM\rangle &= M|JM\rangle \end{aligned} \tag{3}$$

$^{\diamond\diamond}$ For explicit details see D. E. Littlewood, *Theory of Group Characters* page 272

$^{\diamond\diamond\diamond}$ Quasicrystals form an important exception. While locally they may exhibit pentagonal symmetry globally they exhibit a non-periodic symmetry where

$$M = J, J-1, J-2, \ldots - J \tag{4}$$

and J is a positive integer or half-odd integer. It is apparent from Eq.(4) that for a given value of J there are $2J+1$ basis states $|JM\rangle$. We can *ladder* from one state $|JM\rangle$ to any other member of the basis set by use of the ladder operators $J_\pm$ whose action is

$$J_\pm|JM\rangle = \sqrt{J(J+1) - M(M \pm 1)} \quad |JM \pm 1\rangle \tag{5}$$

within the bounds

$$J_+|JJ\rangle = 0 \qquad J_-|J - J\rangle = 0 \tag{6}$$

For the case of *integer* J. here I shall let L denote such angular momenta, the spherical harmonics $Y_M^L(\theta, \phi)$ form a basis for a $2L+1$-dimensional irreducible representation $\mathcal{D}^L$ of SO_3 with the elements of the representation $\mathcal{D}^L_{M,M'}(r, \theta, \phi)$ being the familiar rotation matrices of QTA in spherical coordinates..

■ 3. Characters of SO_3 for Finite Angles of Rotation

⋄ All rotations through the same angle α belong to the same class of SO_3 irrespective of the axis of rotation. For a rotation through an angle α about the $z-$axis we have

$$Y_M^L(\theta, \phi + \alpha) = e^{iM\alpha} Y_M^L(\theta, \phi) \tag{7}$$

Such a rotation can be represented by a rank $(2L+1)$ diagonal matrix with diagonal matrix elements $e^{iM\alpha}$ and hence of trace, or *character*,

$$\begin{aligned}\chi_\alpha^L &= \sum_{M=-L}^{L} e^{iM\alpha} \\ &= \frac{e^{i(L+\frac{1}{2})\alpha} - e^{-i(L+\frac{1}{2})\alpha}}{e^{i\frac{\alpha}{2}} - e^{-i\frac{\alpha}{2}}} \\ &= \frac{\sin\frac{1}{2}(2L+1)\alpha}{\sin\frac{1}{2}\alpha}\end{aligned} \tag{8}$$

The identity element of SO_3 corresponds to a rotation through $\alpha = 0^o$ and hence

$$\chi_0^L = (2L+1) \tag{9}$$

which is just the *dimension* of the irreducible representation $\mathcal{D}^L$.

■ 4. Half-Integer Angular Momentum

So far we have neglected spin and the possibility of half-integer angular momentum. We can use most of our previous results almost unchanged. The basic angular momentum commutation relations are unchanged and we can still produce states $|JM\rangle$ to produce a basis for a $(2J+1)$-dimensional irreducible representation $\mathcal{D}^J$ of SO_3*. Since

$$e^{-i\alpha J_z}|JM\rangle = e^{-i\alpha M}|JM\rangle \tag{10}$$

the characteristics χ_α^J of SO_3 will be exactly as in Eq.(8) except for the replacement of L by J. However, note the important difference - for half-integer values of J the factor

$$e^{-2\pi i M} = -1 \tag{11}$$

and hence for a rotation about a $z-$axis through $\alpha = 2\pi$

$$|JM\rangle \to -|JM\rangle \qquad \alpha = 2\pi \tag{12}$$

This has important consequences since under the usual finite group rotations rotations through 0 and 2π are equivalent making it impossible to form, for half-integer J, linear combinations of $|JM\rangle$ that possess the symmetry of the appropriate finite group rotational symmetry. The solution was given by Bethe in 1929, (with an important correction by Opechowski nearly two decades later) with the introduction of

* Strictly speaking these are irreducible representations of the *covering group* of SO_3, namely SU_2

double groups or perhaps more precisely *extended groups***. In Bethe's case the finite group is augmented with an element $\bar{E}$ which commutes with all the elements of the group and is such that

$$\bar{E}^2 = E \tag{13}$$

This results in additional group elements $\bar{g}$ when

$$\bar{g} = \bar{E} \times g = g \times \bar{E} \quad if \quad \bar{g} \not\equiv g \tag{14}$$

This *may* lead to a doubling of the number of elements to form the extended group (and hence the unfortunate name *double group*) except classes containing rotations through π are often not doubled. Technically these extended groups may also be associated with the fact that they are subgroups of SU_2, the *covering group* of SO_3.

■ 5. Some SO_3 Characters using Maple

It is useful at this stage to collect together the characters χ_α^J for particular angles of interest in making the later connection with finite subgroups. To that end we can write a simple MAPLE programme as overleaf:

** Strictly speaking it is a non-problem. Like the orthogonal groups, O_n and SO_n, finite groups of rotations (or permutations) possess both ordinary tensor representations *and spin* or *projective* representations as indeed recognised long ago by Schur and Frobenius whose use of spin matrices long pre-dates the Pauli spin matrices, originally introduced by Hamilton. However, Bethe's solution is more familiar to physicists

```
A:=proc(a,f,l)
   local x,J;
  x:=sin(1/2*(2*J+1)*a)/sin(1/2*a);
for J from f to l by (1/2) do
 x:=(expand(sin(1/2*(2*J+1)*a)/sin(1/2*a)));
 print(‘J =‘,J,‘ ‘,x);
 od;
end;
```

where a is the angle α expressed in units of π. If f is the smallest value of J and l the largest value of J then the character χ_α^J is computed for all values of J in that range in steps of $\frac{1}{2}$ in J. As an example we give below the output for $\alpha = \frac{2\pi}{5}$ as arises in the case of the groups $\mathcal{I}$ and $\mathcal{D}_5$.

```
> read‘j.fn‘;
--------------------------------------------------------------------
> A(2*Pi/5,0,8);
                                  J =, 0,  , 1
                                                   1/2 1/2
                                             (5 + 5   )
                           J =, 1/2,  , -------------
                                                   1/2 1/2
                                             (5 - 5   )
                                                  1/2 1/2
                                            (5 + 5   )
                            J =, 1,  , -------------
                                                  1/2 1/2
                                            (5 - 5   )
                                 J =, 3/2,  , 1
                                  J =, 2,  , 0
                                 J =, 5/2,  , -1
                                                   1/2 1/2
                                             (5 + 5   )
                           J =, 3,  , - -------------
                                                   1/2 1/2
                                             (5 - 5   )
                                                    1/2 1/2
                                              (5 + 5   )
                          J =, 7/2,  , - -------------
                                                    1/2 1/2
                                              (5 - 5   )
                                  J =, 4,  , -1
                                 J =, 9/2,  , 0
                                  J =, 5,  , 1
```

Continuing we obtain the results given in the following table:-

Table I. The Characteristics χ^J_α for Special Angles

J	C_2	C_3	C_3^2	C_4	C_5	C_5^2
0	1	1	1	1	1	1
1/2	0	1	-1	$\sqrt{2}$	$(\sqrt{5}+1)/2$	$-(1-\sqrt{5})/2$
1	-1	0	0	1	$(\sqrt{5}+1)/2$	$(1-\sqrt{5})/2$
3/2	0	-1	1	0	1	-1
2	1	-1	-1	-1	0	0
5/2	0	0	0	$-\sqrt{2}$	-1	1
3	-1	1	1	-1	$-(\sqrt{5}+1)/2$	$-(1-\sqrt{5})/2$
7/2	0	1	-1	0	$-(\sqrt{5}+1)/2$	$(1-\sqrt{5})/2$
4	1	0	0	1	-1	-1
9/2	0	-1	1	$\sqrt{2}$	0	0
5	-1	-1	-1	1	1	1
11/2	0	0	0	0	$(\sqrt{5}+1)/2$	$-(1-\sqrt{5})/2$
6	1	1	1	-1	$(\sqrt{5}+1)/2$	$(1-\sqrt{5})/2$
13/2	0	1	-1	$-\sqrt{2}$	1	-1
7	-1	0	0	-1	0	0
15/2	0	-1	1	0	-1	1
8	1	-1	-1	1	$-(\sqrt{5}+1)/2$	$-(1-\sqrt{5})/2$

■ 6. Some Extended Group Character Tables

For future use I now give some of the character tables for the extension of a number of relevant point groups.

Table II. Characters of the Spin Representations of $\mathcal{I}$

$$\begin{array}{c} \\ E' \\ E'' \\ U' \\ W' \end{array}
\begin{array}{ccccccccc} E & \bar{E} & 20C_3 & 20C_3\bar{E} & 30C_2 & 12C_5 & 12C_5\bar{E} & 12C_5^2 & 12C_5^2\bar{E} \\
\end{array}$$

$$\begin{array}{c|ccccccccc}
 & E & \bar{E} & 20C_3 & 20C_3\bar{E} & 30C_2 & 12C_5 & 12C_5\bar{E} & 12C_5^2 & 12C_5^2\bar{E} \\
\hline
E' & 2 & -2 & 1 & -1 & 0 & \frac{1}{2}(1+\sqrt{5}) & -\frac{1}{2}(1+\sqrt{5}) & -\frac{1}{2}(1-\sqrt{5}) & \frac{1}{2}(1-\sqrt{5}) \\
E'' & 2 & -2 & 1 & -1 & 0 & \frac{1}{2}(1-\sqrt{5}) & -\frac{1}{2}(1-\sqrt{5}) & -\frac{1}{2}(1+\sqrt{5}) & \frac{1}{2}(1+\sqrt{5}) \\
U' & 4 & -4 & -1 & 1 & 0 & 1 & -1 & -1 & 1 \\
W' & 6 & -6 & 0 & 0 & 0 & -1 & 1 & 1 & -1
\end{array}$$

Table III. Characters of the Spin Representations of $\mathcal{D}_5$

$$\begin{array}{cc|cccccccc}
 & & E & \bar{E} & 2C_5 & 2C_5\bar{E} & 2C_5^2 & 2C_5^2\bar{E} & 5C_2 & 5C_2\bar{E} \\
\hline
E' & & 2 & -2 & (1+\sqrt{5})/2 & -(1+\sqrt{5})/2 & -(1-\sqrt{5})/2 & (1-\sqrt{5})/2 & 0 & 0 \\
E'' & & 2 & -2 & (1-\sqrt{5})/2 & -(1-\sqrt{5})/2 & -(1+\sqrt{5})/2 & (1+\sqrt{5})/2 & 0 & 0 \\
E'''\{ & \rho_1 & 1 & -1 & -1 & 1 & 1 & -1 & i & -i \\
 & \rho_2 & 1 & -1 & -1 & 1 & 1 & -1 & -i & i
\end{array}$$

Table IV. Characters of the Spin Representations of $\mathcal{T}$

$$\begin{array}{cc|ccccccc}
 & & E & \bar{E} & 6C_2 & 4C_3 & 4C_3\bar{E} & 4C_3' & 4C_3'\bar{E} \\
\hline
E' & & 2 & -2 & 0 & 1 & -1 & -1 & 1 \\
U'\{ & E'' & 2 & -2 & 0 & \omega & -\omega & -\omega^2 & \omega^2 \\
 & E''' & 2 & -2 & 0 & \omega^2 & -\omega^2 & -\omega & \omega
\end{array}$$

■ 7. $SO_3 \to \mathcal{I}$ Branching Rules

The reduction from spherical to icosahedral symmetry and the lifting of the $(2J+1)-$fold degeneracy comes from a knowledge of the $SO_3 \to \mathcal{I}$ branching rules. These may be readily calculated by knowing the characteristics for SO_3 for the relevant angles associated with the $\mathcal{I}$ group and the character table for $\mathcal{I}$ to yield the results given below

Table V. Branching Rules for $SO(3) \rightarrow \mathcal{I}$

J	$\mathcal{I}$
0	A
1	T_1
2	V
3	$T_2 + U$
4	$U + V$
5	$T_1 + T_2 + V$
6	$A + T_1 + U + V$
7	$T_1 + T_2 + U + V$
8	$T_2 + U + 2V$
9	$T_1 + T_2 + 2U + V$
10	$A + T_1 + T_2 + U + 2V$
11	$2T_1 + T_2 + U + 2V$
12	$A + T_1 + T_2 + 2U + 2V$
13	$T_1 + 2T_2 + 2U + 2V$
14	$T_1 + T_2 + 2U + 3V$
15	$A + 2T_1 + 2T_2 + 2U + 2V$
$\frac{1}{2}$	E'
$\frac{3}{2}$	U'
$\frac{5}{2}$	W'
$\frac{7}{2}$	$E'' + W'$
$\frac{9}{2}$	$U' + W'$
$\frac{11}{2}$	$E' + U' + W'$
$\frac{13}{2}$	$E' + E'' + U' + W'$
$\frac{15}{2}$	$U' + 2W'$

Inspection of the above listing leads to several important conclusions:

1. A $d-$orbital remains degenerate in a field of icosahedral symmetry.
2. A $f-$orbital splits into two sublevels $(T_2 + U)$ of orbital degeneracy 3 and 4 respectively.
3. The identity irreducible representation of $\mathcal{I}$ occurs for $J = 0,\ 6,\ 10,\ 12,\ 15$ and then just once in each case.
4. It is possible for a state of *higher* J to split into *fewer* levels than one of *lower* J.

8. Branching Rules for some Subgroups of $\mathcal{I}$

If the symmetry is lowered from I to one of its subdgroups degeneracies may be further reduced. Again this is determined by a knowledge of the branching rules. We list below a table of some of the relevant branching rules.

Table VI. Branching Rules for the restriction of $\mathcal{I}$ to Major Subgroups

	$\mathcal{T}$	$\mathcal{D}_5$	$\mathcal{D}_3$	$\mathcal{D}_2$
A	A_1	A_1	A_1	A_1
T_1	T	A_2+E_1	A_1+E	$B_1+B_2+B_3$
T_2	T	A_2+E_2	A_2+E	$B_1+B_2+B_3$
U	A_1+T	E_1+E_2	A_1+A_2+E	$A_1+B_1+B_2+B_3$
V	$E+T$	$A_1+E_1+E_2$	A_1+2E	$2A_1+B_1+B_2+B_3$
E'	E'	E'	E'	E'
E''	E'	E''	E'	E'
U'	U'	$E'+E''$	$2E'$	
W'	$E'+U'$	$E'+E'''$	$2E'+E''$	$3E'$

9. Kronecker Products

Kronecker products play an important role in determining selection rules. It is often important to be able to separate the Kronecker square of an irreducible representation into its symmetric and antisymmetric parts. Below we enclose the symmetric part in {} brackets and the antisymmetric part in [] brackets.

Table VII. Kronecker Products for Ordinary Representations of I

	A	T_1	T_2	U	V
A	A	T_1	T_2	U	V
T_1	T_1	$\{A+V\}+[T_1]$	$U+V$	T_2+U+V	T_1+T_2+U+V
T_2	T_2	$U+V$	$\{A+V\}+[T_2]$	T_1+U+V	T_1+T_2+U+V
U	U	T_2+U+V	T_1+U+V	$\{A+U+V\}+[T_1+T_2]$	T_1+T_2+U+2V
V	V	T_1+T_2+U+V	T_1+T_2+U+V	T_1+T_2+U+2V	$\{A+U+2V\}+[T_1+T_2+U]$

Table VIII. Kronecker Products for Spin Representations of I

	E'	E''	U'	W'
A	E'	E''	U'	W'
T_1	$E'+U'$	W'	$E'+U'+W'$	$E''+U'+2W'$
T_2	W'	$E''+U'$	$E''+U'+W'$	$E'+U'+2W'$
U	$E''+W'$	$E'+W'$	$U'+2W'$	$E'+E''+2U'+2W'$
V	$U'+W'$	$U'+W'$	$E'+E''+U'+2W'$	$E'+E''+2U'+3W'$
E'	$A+T_1$	U	T_1+V	T_2+U+V
E''	U	$A+T_2$	T_2+V	T_1+U+V
U'	T_1+V	T_2+V	$A+T_1+T_2+U+V$	$T_1+T_2+2U+2V$
W'	T_2+U+V	T_1+U+V	$T_1+T_2+2U+2V$	$A+2T_1+2T_2+2U+3V$

10. Kronecker Products and Branching Rules

A knowledge of Kronecker products can readily lead to a simple method for recursively extending branching rule tables such as those of Table V. Suppose we need the branching rule for $J=16$. We know from QTA that

$$\mathcal{D}^J \times \mathcal{D}^{J'} = \mathcal{D}^{J+J'} + \mathcal{D}^{J+J'-1} + \ldots + \mathcal{D}^{|J-J'|} \tag{15}$$

and hence

$$\mathcal{D}^1 \times \mathcal{D}^{J'} = \mathcal{D}^{J+1} + \mathcal{D}^{J} + \mathcal{D}^{J-1} \tag{16}$$

We know from Table V that under $SO_3 \to \mathcal{I}$ we have for

$$J = 1\ [1] \to T_1 \tag{17}$$

while for

$$J = 15\ [15] \to A + 2T_1 + 2T_2 + 2U + 2V \tag{18}$$

Taking the Kronecker product of Eq. (17) with Eq. (18), using Table V gives

$$2A + 5T_1 + 4T_2 + 6U + 8V \tag{19}$$

Noting Eq.(16) we need to subtract the branching rules for $J = 14$ and 15 from Eq. (19) to leave

$$J = 16\ [16] \to A + 2T_1 + T_2 + 2U + 3V \tag{20}$$

Adding the dimensions of the $\mathcal{I}$ irreducible representations gives 33 which is the dimension of the [16] irreducible representation of SO_3 Note that we have obtained the identity irrep A in the branching rule. This observation will assume importance in the next lecture.

High Symmetry States with Examples

B. G. Wybourne

A monographic series of six lectures

■ Lecture 4

■ 1. Introduction

In the previous lecture we studied the third-order invariant of the tetrahedral group $\mathcal{T}$ and concluded with the construction of a fourth-order invariant. In this lecture we shall first briefly consider the sixth-order invariants for the group $\mathcal{T}$ and then show how we can obtain from these the sixth-order invariants for the icosahedral group $\mathcal{I}$.

■ 2. First look at Integrity Bases

A homogeneous polynomial $P_G^m(\alpha)$ of degree m in n variables $\alpha_1, \alpha_2, \ldots, \alpha_n$ is said to be an *invariant* of a group G if for all group transformations $T(g) \quad (g \in G)$ we have

$$P_G^m[T(g)\alpha] \equiv P_G^m(\alpha) \tag{1}$$

A fundamental problem, long recognised in the theory of invariants, is to determine the minimal set $P_G[\alpha]$ of invariant polynomials associated with a given group G in terms of which all other invariant polynomials may be generated. Such a minimal set of invariants will be said to form an *integral rational basis* or *integrity basis*.

The choice of an integrity basis for a given group G is not unique. Different integrity bases are associated with the various subgroups H of G. Further, a given subgroup H of G may often be embedded in G in several different ways giving rise to different integrity bases. In many cases there is value in constructing integrity bases symmetrised with respect to the various subgroups of a given group G. For example, we may construct integrity bases for the icosahedral group $\mathcal{I}$ from those found for the subgroups $\mathcal{D}_5$, $\mathcal{T} \supset \mathcal{D}_2$ or $\mathcal{T} \supset \mathcal{C}_3$.

■ 3. Invariant States for $\mathcal{D}_n$ and $\mathcal{C}_n$

The cyclic groups $\mathcal{C}_n$ are Abelian and involve n pure rotations about an $n-$fold axis. We shall choose this axis as the z axis. The dihedral groups $\mathcal{D}_n$ are formed from C_n by adding a $2-$fold rotation perpendicular to the $z-$axis to give a group containing $2n$ elements. Here we seek integrity bases such that each member of a given set can be associated with a particular J value associated with the SO_3 Casimir invariant $\mathbf{J}^2$ and demand that our invariants be Hermitian.

The invariants for a given group $\mathcal{C}_n$ may be constructed for the $|JM\rangle$ kets by standard application of the rotation operators of $\mathcal{C}_n$ to the kets. The integrity basis for a given $\mathcal{C}_n$, with $n > 1$, involves just four members which can be chosen as

$$\mathcal{C}_n : \quad |00\rangle,\ |10\rangle,\ (|n,n\rangle + (-1)^n|n,-n\rangle)\ i(|n,n\rangle - (-1)^n|n,-n\rangle) \tag{2}$$

The integrity bases for the dihedral groups $\mathcal{D}_n$, with $n \geq 2$, likewise involve just four members which may be chosen as

$$\mathcal{D}_n : \quad |00\rangle,\ |20\rangle,\ (|n,n\rangle + (-1)^n|n,-n\rangle)\ i(|n+1,n\rangle - (-1)^n|n+1,-n\rangle) \tag{3}$$

In both cases higher-order invariant kets may be constructed from the members of the integrity bases by standard angular momentum coupling.

Alternative integrity bases for $\mathcal{C}_n$ and $\mathcal{D}_n$ can be defined by taking suitable linear combinations of the members of a given integrity basis.

■ 4. Invariant Operators for $\mathcal{C}_n$ and $\mathcal{D}_n$

The construction of invariant *operators* for the cyclic and dihedral groups follow immediately from recognising the similarity under transformations of kets and operators

$$|kq\rangle \Leftrightarrow T_q^{(k)} \tag{4}$$

leading to

$$\mathcal{C}_n : \quad T_0^{(0)},\ T_0^{(1)},\ T_n^{(n)} + (-1)^n T_{-n}^{(n)},\ i(T_n^{(n)} - (-1)^n T_{-n}^{(n)}) \tag{5}$$

and

$$\mathcal{D}_n: \quad T_0^{(0)},\ T_0^{(2)},\ T_n^{(n)} + (-1)^n T_{-n}^{(n)},\ i(T_n^{(n+1)} - (-1)^n T_{-n}^{(n+1)}) \tag{6}$$

There is an important difference between invariant states and invariant operators, the latter generally do not commute. The commutator of an invariant is itself an invariant and hence all four members of the sets of invariant operators are not independent. The minimal set of invariant operators can always be chosen as consisting of $T_0^{(0)}$ and any to of the remaining invariant operators. This set of three independent invariant operators suffice to generate all other invariant operators. Clearly $T_0^{(0)}$ commutes with all other invariant operators.

■ 5. Integrity bases for the Tetrahedral Group $\mathcal{T}$

The branching rules given below show that we can expect three invariants of $\mathcal{T}$ associated with $J = 0,\ 3,\ 4$ and two with $J = 6$. However one of the invariants for $J = 6$ is not an independent invariant since one can be represented in terms of the square of the third-order invariant. Note that unlike for $\mathcal{D}_2$ there is no second-order invariant.

J	$\mathcal{T}$
0	A_1
1	T
2	$E + T$
3	$A_1 + 2T$
4	$A_1 + E + 2T$
5	$E + 3T$
6	$2A_1 + E + 3T$

Table I. Some $SO_3 \to \mathcal{T}$ Branching Rules

The $\mathcal{T} \to \mathcal{D}_2$ branching rules below give us a clue as to the construction of the $\mathcal{T}$ invariants.

$\mathcal{T}$	$\mathcal{D}_2$
A_1	A_1
E	$2A_1$
T	$B_1 + B_2 + B_3$

Table II. $\mathcal{T} \to \mathcal{D}_2$ Branching Rules

Recall that the minimal set of invariants for $\mathcal{D}_2$ involves

$$T_0^{(0)},\ T_0^{(2)},\ (T_2^{(2)} + T_{-2}^{(2)}),\ i(T_2^{(3)} - T_{-2}^{(3)}) \tag{7}$$

The third-order invariant of $\mathcal{D}_2$ is also the third-order invariant of $\mathcal{T}$. The fourth-order invariant of $\mathcal{T}$ will be a certain linear combination of the dependent fourth-order invariants $T_0^{(4)}$ and $(T_4^{(4)} + T_{-4}^{(4)})$. Indeed as we found in the previous lecture we may take

$$X_4^{\mathcal{T}} = \mathcal{N}(T_0^{(4)} + \frac{\sqrt{70}}{14}(T_4^{(4)} + T_{-4}^{(4)}) \tag{8}$$

where $\mathcal{N}$ is a suitable normalisation constant.

An integrity basis for $\mathcal{T} \supset \mathcal{C}_3$ can be obtained from the one for $\mathcal{T} \supset \mathcal{D}_2$ by a rotation through $\frac{\pi}{4}$ about the $z-$axis followed by a rotation through $\beta = cos^{-1}(\frac{1}{\sqrt{3}})$ about the new $y-$axis. This amounts to shifting the $z-$axis from the [001] direction to the [111] direction. The groups $\mathcal{C}_3$ and $\mathcal{D}_2$ may be embedded in the group $\mathcal{T}$ in different ways, each giving rise to different integrity bases. These different embeddings amount to different choices of axes and usually do no more than change the signs of the invariants of degree $3,\ 4,\ 6$.

The difference between the integrity bases for $\mathcal{T} \supset \mathcal{D}_2$ and $\mathcal{T} \supset \mathcal{C}_3$ is seen in the fact that while the third-order invariant for $\mathcal{D}_2$ is also the third-order invariant for $\mathcal{T}$ such is not the case for $\mathcal{C}_3$. Specifically we find the independent state invariants as

$$\mathcal{T} \supset \mathcal{D}_2 |00\rangle,\ i(|32\rangle - |3-2\rangle), |40\rangle + \frac{\sqrt{70}}{14}(|44\rangle + |4-4\rangle)$$
$$(|62\rangle + |6-2\rangle - \frac{\sqrt{55}}{11}(|66\rangle + |6-6\rangle) \tag{9}$$

and

$$\mathcal{T} \supset \mathcal{C}_3 |00\rangle,\ |30\rangle + \frac{\sqrt{10}}{5}(|33\rangle - |3-3\rangle,\ |40\rangle - \frac{\sqrt{70}}{7}(|43\rangle - |4-3\rangle)$$
$$i\left((|63 + |6-3\rangle) + \frac{\sqrt{110}}{22}(|66\rangle - |6-6\rangle)\right) \tag{10}$$

The corresponding tensor operator invariant follow upon making the substitution

$$|kq\rangle \to T_q^{(k)} \tag{11}$$

remebering though that the tensor operators are generally non-commutative. In Eq. (9) we have taken the $z-$axis in the [001] direction and in Eq. (10) in the [111] direction.

The additional sixth-order invariant for $\mathcal{T}$ can be found from squaring the third-order invariant to give

$$\mathcal{T} \supset \mathcal{D}_2 : |60\rangle - \frac{\sqrt{14}}{2}(|64\rangle + |6-4\rangle) \tag{12}$$

and

$$\mathcal{T} \supset \mathcal{C}_3 : |60\rangle + \frac{\sqrt{210}}{24}(|63\rangle - |6-3\rangle) + \frac{\sqrt{231}}{24}(|66\rangle + |6-6\rangle) \tag{13}$$

The eigenvaluse and degeneracies of the operators are invariant with respect to changes in the relative signs that occur upon rotation to another set of equivalent axes, however the associated eigenvectors may be quite different.

■ 6. Integrity Bases and Invariant Operators for the Octahedral Group

The integrity basis for $\mathcal{O}$ involves invariants of order 0, 4, 6, 9. The fourth and sixth order invariants of $\mathcal{T}$ given in Eqs. (9) and (12) respectively for $\mathcal{T} \supset D_2$ are also invariants of $\mathcal{O}$ and likewise in Eqs. (10) and (13) for $\mathcal{T} \supset \mathcal{C}_3$. However, the third- and sixth-order invariants of $\mathcal{T}$ given in Eqs. (9) and (10) are NOT invariants of $\mathcal{O}$ but transform under $\mathcal{O}$ as the Γ_2 irreducible representation of $\mathcal{O}$. Since $\Gamma_2 \times \Gamma_2 = \Gamma_1$ the products of these third- and sixth-order invariants of $\mathcal{T}$ must yield invariants under $\mathcal{O}$. Under $SO_3 \to \mathcal{O}$ we find the identity irrep Γ_1 of $\mathcal{O}$ occurs just once and hence there must be a ninth-order invariant that may be formed by coupling of the third- and sixth-order invariants of $\mathcal{T}$ leading to the octahedral integrity basis states as

$$\mathcal{O} \supset \mathcal{T} \supset D_2 : |00\rangle,\ |40\rangle + \frac{\sqrt{70}}{14}(|44\rangle + |4-4\rangle),\ |60\rangle - \frac{\sqrt{14}}{2}(|64\rangle + |6-4\rangle),$$
$$i\left((|94\rangle - |9-4\rangle - \frac{\sqrt{119}}{7}(|98\rangle - |9-8\rangle)\right) \tag{14}$$

and

$$\mathcal{O} \supset \mathcal{T} \supset \mathcal{C}_3 : |00\rangle,\ |40\rangle - \frac{\sqrt{70}}{7}(|43\rangle - |4-3\rangle),\ |60\rangle + \frac{\sqrt{210}}{24}(|63\rangle - |6-3\rangle) + \frac{\sqrt{231}}{24}(|66\rangle + |6-6\rangle),$$
$$i\left((|93\rangle + |9-3\rangle - 2\frac{\sqrt{663}}{221}(|99\rangle + |9-9\rangle)\right) \tag{15}$$

7. The Icosahedral Group Again

As already noted the icosahedral group has invariants of order 0, 6, 10, 15. The $z-$axis may be chosen in many different ways. Choosing the $z-$axis as a $5-$fold axis corresponds to the group-subgroup scheme $SO_3 \supset \mathcal{I} \supset \mathcal{D}_5$ whereas choosing the $z-$axis as a $2-$fold or $3-$fold axis corresponds to the group-subgroup schemes $SO_3 \supset \mathcal{I} \supset \mathcal{D}_2$ and $SO_3 \supset \mathcal{I} \supset \mathcal{C}_3$ respectively. Furthermore, the tetrahedral group $\mathcal{T}$ occurs as a physically important subgroup of $\mathcal{I}$ giving rise to the group-subgroup combinations $\mathcal{I} \supset \mathcal{T} \supset \mathcal{D}_2$ and $\mathcal{I} \supset \mathcal{T} \supset \mathcal{C}_3$.

It suffices to construct just the sixth-order invariants as the tenth- and fifteenth-order invariants can be constructed from these by a building up procedure. The icosahedral invariants must involve certain linear combinations of the corresponding sixth-order invariants associated with the relevant subgroups. These linear conmbinations may be determined either from the action of the rotation operators of the group $\mathcal{I}$ that lie outside of the relevant subgroups or by diagonalising a linear combination of sixth-order operator invariants with the coefficients of the linear combination treated as a parameter to be fixed by the requirement that the eigenvalues have the required degeneracies for $\mathcal{I}$ symmetry.

Thus we have the possible linear combinations:-

$$\mathcal{I} \supset \mathcal{D}_5 : |60\rangle + ix(|65\rangle + |6-5\rangle) \tag{16}$$

$$\mathcal{I} \supset \mathcal{T} \supset \mathcal{D}_2 : |60\rangle - \frac{\sqrt{14}}{2}(|64\rangle + |6-4\rangle) + y\left((|62\rangle + |6-2) - \frac{\sqrt{55}}{11}(|66\rangle + |6-6)\right) \tag{17}$$

$$\begin{aligned}\mathcal{I} \supset \mathcal{T} \supset \mathcal{C}_3 : &|60\rangle + \frac{\sqrt{210}}{24}(|63\rangle - |6-3\rangle) + \frac{\sqrt{231}}{24}(|66\rangle + |6-6\rangle) \\ &+ iz\left((|63 + |6-3\rangle) + \frac{\sqrt{110}}{22}(|66\rangle - |6-6\rangle)\right)\end{aligned} \tag{18}$$

The coefficients x, y, z may be readily determined by diagonalising the sixth-order invariant operators in a $J = 3$ manifold of states $|3M\rangle$ and demanding that the numbers x, y, z be chosen so as to yield just two distinct eigenvalues, one of degeneracy three and one of degeneracy four in accord with the branching rule $\mathcal{D}^{(3)} \to U + V$ for the icosahedral group $\mathcal{I}$. Thus for the case of the operator equivalent of Eq. (16) we find three $2-$fold degenerate eigenvalues

$$-\frac{75\sqrt{231}}{54} \pm 15\sqrt{\frac{21}{44} + 18x^2},\ \frac{225\sqrt{231}}{77}$$

and the single degenerate eigenvalue

$$-\frac{300\sqrt{231}}{77}$$

There are two ways of combining these to obtain the degeneracies of icosahedral symmetry. These yield

$$x = \pm\frac{\sqrt{77}}{11} \tag{19}$$

In precisely the same manner we find

$$y = \pm\frac{\sqrt{330}}{22} \tag{20}$$

and

$$z = \pm\frac{3\sqrt{14}}{8} \tag{21}$$

The ambiquity of sign has no physical consequences provided the choice is made and then applied consistently throughout all practical calculations. As in all quantum calculations the mixing of phase conventions is not permitted. Effectively the difference in sign depends on our choice of the direction of the x, y axes relative to the icosahedron.

By way of example we give the tenth-order invariant for $SO_3 \supset \mathcal{T} \supset \mathcal{D}_5$ as

$$|10,0\rangle \mp i\frac{\sqrt{429}}{13}(|10,5\rangle + |10,-5\rangle) - \frac{\sqrt{46189}}{247}(|10,10\rangle + |10,-10\rangle) \tag{22}$$

■ 8. Construction of Symmetrised and Labelled States

We now consider as an explicit example the construction of a set of states symmetrised according to the group chain $SO_3 \supset \mathcal{I} \supset \mathcal{D}_5$. We shall take the sixth-order invariant as

$$X = \sqrt{3003}\left(U_0^{(6)} + \frac{i\sqrt{77}}{11}(U_5^{(6)} + U_{-5}^{(6)})\right) \tag{23}$$

where the factor $\sqrt{3003}$ has been chosen to produce simple eigenvalues. The matrix elements of X may be evaluated in a $|LM\rangle$ basis using the Wigner-Eckart theorem and the Nielson-Koster tables for the doubly reduced matrix elements.

Let us first consider the case of a single $f-$electron in an icosahedral field and ignore spin-orbit effects. This amounts to the strong icosahedral case. Under $SO_3 \to \mathcal{I}$ we have

$$^2F \to^2 (T_2 + U) \tag{24}$$

The states of the f^n configuration, in the strong field approximation would involve occupancy of t_2 and u orbitals. To obtain the appropriate linear combinations of $|LM\rangle$ states we may diagonalise the operator X within the set of states $|3M\rangle \qquad M = 0,\ \pm1,\ \pm2,\ \pm3$. We readily find the matrix elements as

$$\langle 30|X|30\rangle = -10,\ \langle 3\pm1|X|3\pm1\rangle = \frac{15}{2} \tag{25}$$

and

$$\begin{array}{cc} & \begin{array}{cc} |3\pm2\rangle & |3\mp3\rangle \end{array} \\ \begin{array}{c} \langle 3\pm2| \\ \langle 3\mp3| \end{array} & \begin{bmatrix} -3 & \frac{7\sqrt{-6}}{2} \\ -\frac{7\sqrt{-6}}{2} & \frac{1}{2} \end{bmatrix} \end{array} \tag{26}$$

Diagonalising the above matrix yields the eigenvalues $\frac{15}{2},\ -10$ with eigenvectors

$$|-10\rangle = \frac{1}{\sqrt{5}}(-i\sqrt{3}|3\pm2\rangle + \sqrt{2}|3\mp3\rangle) \tag{27}$$

$$|\frac{15}{2}\rangle = \frac{1}{\sqrt{5}}(i\sqrt{2}|3\pm2\rangle + \sqrt{3}|3\mp3\rangle) \tag{28}$$

Note that the eigenvalue -10 occurs in the above cases with a degeneracy of 3 and hence may be associated with the three-fold degenerate irreducible representation T_2 of $\mathcal{I}$ while the eigenvalue $\frac{15}{2}$ occurs with a degeneracy of 4 and may be associated with the four-fold degenerate irreducible representation U of $\mathcal{I}$ and hence the symmetrised states for a single $f-$electron will be:-

$$\begin{aligned} |T_2,1\rangle &= |30\rangle \\ |T_2,2\rangle &= \frac{1}{\sqrt{5}}(-i\sqrt{3}|32\rangle + \sqrt{2}|3-3\rangle) \\ |T_2,3\rangle &= \frac{1}{\sqrt{5}}(-i\sqrt{3}|3-2\rangle + \sqrt{2}|33\rangle) \end{aligned} \tag{29}$$

and

$$\begin{aligned} |U,1\rangle &= |31\rangle \\ |U,2\rangle &= |3-1\rangle \\ |U,3\rangle &= \frac{1}{\sqrt{5}}(i\sqrt{2}|32\rangle + \sqrt{3}|3-3\rangle) \\ |U,4\rangle &= \frac{1}{\sqrt{5}}(i\sqrt{2}|3-2\rangle + \sqrt{3}|33\rangle) \end{aligned} \tag{30}$$

Now consider the case of a pair of $f-$electrons with maximum spin $S = 1$. In the strong field case we have the icosahedral configurations u^2, ut_2 and t_2^2 configurations. The possible icosahedral states in u^2 will involve those $\mathcal{I}$ irreducible representations that occur in the antisymmetric part of the Kronecker square of U; in ut_2 those in the Kronecker product $U \times T_2$; in t_2^2 those in the antisymmetric part of the Kronecker square of T_2. Thus we have:

$$\begin{aligned} {}^3u^2 &\supseteq T_1 + T_2 \\ {}^3ut_2 &\supseteq T_1 + U + V \\ {}^3t_2^2 &\supseteq T_2 \end{aligned} \tag{31}$$

The states associated with the above irreducible representations of $\mathcal{I}$ will, in a $LS-$coupling basis involve linear combinations of the $|LM\rangle$ that derive from the triplet terms ${}^3P$, ${}^3F$, ${}^3H$ of the f^2 configuration. To obtain the coefficients of these linear combinations we may diagonalise the sixth-order operator given in Eq. (23). To that end it is useful to organise the basis states as follows:-

$$\begin{aligned} \mu = 0 &: -|10\rangle,\ |30\rangle,\ |50\rangle,\ |55\rangle_+,\ |55\rangle_- \\ \mu = \pm 1 &: -|1 \pm 1\rangle,\ |3 \pm 1\rangle,\ |5 \pm 1\rangle,\ |5 \mp 4\rangle \\ \mu = \pm 2 &: -|3 \pm 2\rangle,\ |3 \mp 3\rangle,\ |5 \pm 2\rangle,\ |5 \mp 3\rangle \end{aligned} \tag{32}$$

Thus we need to evaluate the matrices for each set of basis states, diagonalise them obtaining their eigenvalues and eigenvalues as below

- $\mu = 0$

$$\begin{array}{c} \\ \langle 1,0| \\ \langle 3,0| \\ \langle 5,0| \\ \langle 5,5|_+ \\ \langle 5,5|_- \end{array} \begin{array}{c} \begin{array}{ccccc} |1,0\rangle & |3,0\rangle & |5,0\rangle & |5,5\rangle_+ & |5,5\rangle_- \end{array} \\ \left[\begin{array}{ccccc} 0 & 0 & 3\sqrt{3} & -\frac{i\sqrt{42}}{2} & 0 \\ 0 & \frac{10}{3} & -\frac{7\sqrt{14}}{3} & -14i & 0 \\ 3\sqrt{3} & -\frac{7\sqrt{14}}{3} & \frac{20}{3} & -\frac{5i\sqrt{14}}{2} & 0 \\ \frac{i\sqrt{42}}{2} & 14i & \frac{5i\sqrt{14}}{2} & -\frac{5}{2} & 0 \\ 0 & 0 & 0 & 0 & -\frac{5}{2} \end{array}\right] \end{array}$$

Eigenvalues

$$-\frac{5}{2} \qquad ,15 \qquad ,15 \qquad ,-20 \qquad ,-\frac{5}{2}$$

Eigenvectors

$$\begin{bmatrix} .92582 & -.35220 & .13713 & 0 & 0 \\ 0 & .29624 & .76085 & -.57735 & 0 \\ -.32071 & -.84289 & .00034 & -.43204 & 0 \\ -.2i & -.27876i & .63426i & .69282i & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}$$

■ $\mu = \pm 1$

$$\begin{array}{c} \\ \langle 1,\pm1| \\ \langle 5,\pm1| \\ \langle 5,\mp4| \\ \langle 3,\pm1| \end{array} \begin{array}{c} \begin{array}{cccc} |1,\pm1\rangle & |5,\pm1\rangle & |5,\mp4\rangle & |3,\pm1\rangle \end{array} \\ \left[\begin{array}{cccc} 0 & -\frac{3\sqrt{5}}{2} & \frac{i\sqrt{105}}{2} & 0 \\ -\frac{3\sqrt{5}}{2} & 2 & -\frac{3i\sqrt{21}}{2} & 0 \\ -\frac{i\sqrt{105}}{2} & \frac{3i\sqrt{21}}{2} & 8 & 0 \\ 0 & 0 & 0 & -\frac{5}{2} \end{array}\right] \end{array}$$

Eigenvalues

$$-\frac{5}{2} \quad ,15 \quad ,-\frac{5}{2} \quad ,-\frac{5}{2}$$

Eigenvectors

$$\begin{bmatrix} -.92582 & -.37796 & .42857 & 0 \\ -.20701 & .50709 & -.74082 & 0 \\ -.31622i & .77459i & .69410i & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

■ $\mu = \pm 2$

$$\begin{array}{c} \\ \langle 3,\pm2| \\ \langle 3,\mp3| \\ \langle 5,\pm2| \\ \langle 5,\mp3| \end{array} \begin{array}{c} \begin{array}{cccc} |3,\pm2\rangle & |3,\mp3\rangle & |5,\pm2\rangle & |5,\mp3\rangle \end{array} \\ \left[\begin{array}{cccc} -\frac{1}{6} & \frac{7i\sqrt{6}}{6} & -\frac{14\sqrt{2}}{3} & \frac{14i\sqrt{3}}{3} \\ -\frac{7i\sqrt{6}}{6} & 1 & \frac{14i\sqrt{3}}{3} & 7\sqrt{2} \\ -\frac{14\sqrt{2}}{3} & -\frac{14i\sqrt{3}}{3} & -\frac{29}{6} & \frac{7i\sqrt{6}}{6} \\ -\frac{14i\sqrt{3}}{3} & 7\sqrt{2} & -\frac{7i\sqrt{6}}{6} & -6 \end{array}\right] \end{array}$$

Eigenvalues

$$15 \quad ,-20 \quad ,-\frac{5}{2} \quad ,-\frac{5}{2}$$

Eigenvectors

$$\begin{bmatrix} .51639 & -.36514 & .74053 & .40804 \\ -.63245i & .44721i & .60464i & .33317i \\ -.36514 & -.51639 & -.22715 & .68505 \\ -.44721i & -.63245i & .18547i & -.55934i \end{bmatrix}$$

First note that the eigenvalues have the values and degeneracies (given in () brackets)

$$t_2^2 - 20(3),\ ut_2 : \frac{-5}{2}(12),\ u^6 : 15(6) \tag{33}$$

These may be associated with the two-electron icosahedral configurations given in Eq. (31) as shown above. Note that the degeracies obtained are precisely those expected from the $\mathcal{I}$ content of the respective configurations. The eigenvectors give the linear combinations of the $|LM\rangle$ states. An equivalent, but possibly more instructive, basis could have been obtained by first diagonalising the sixth-order operator for the triplet terms ${}^3PFH$ and then using these as icosahedrally symmetrised basis functions. Use of MAPLE readily leads to the results:

■ ${}^3P \qquad {}^3T_1$

All matrix elements of X are zero and hence

$$|{}^3P\ T_1\ 0\rangle = |10>, \quad |{}^3P\ T_1\ \pm 1\rangle = |1 \pm 1> \tag{34}$$

■ $^3F \qquad ^3(T_2 + U)$

The eigenvalue $\frac{10}{3}$ occurs with a degeneracy 3 and $-\frac{5}{2}$ with a degeneracy 4 and hence the latter are associated with the ^3U and the former with $^3T_2$ leading to the eigenvectors

$$\begin{aligned} |^3F\ T_2\ 0\rangle &= |30\rangle \\ |^3F\ T_2\ \pm 2\rangle &= \frac{1}{\sqrt{5}}\left[i\sqrt{2}|3\pm 2\rangle + \sqrt{3}|3\mp 3\rangle\right] \end{aligned} \tag{35}$$

and

$$\begin{aligned} |^3F\ U\ \pm 1\rangle &= |3\pm 1\rangle \\ |^3F\ U\ \pm 2\rangle &= \frac{1}{\sqrt{5}}\left[-i\sqrt{3}|3\pm 2\rangle + \sqrt{2}|3\mp 3\rangle\right] \end{aligned} \tag{36}$$

■ $^3H \qquad ^3(T_1 + T_2 + V$

Three eigenvalues $\frac{25}{2}(3)[^3T_1]$, $-\frac{25}{3}(3)[^3T_2]$, $-\frac{5}{2}(5)[^3V]$ are obtained with associated eigenvectors

$$\begin{aligned} |^3H\ T_1\ 0\rangle &= \frac{1}{5}\left[3\sqrt{2}|50\rangle + i\sqrt{7}|55\rangle_+\right] \\ |^3H\ T_1\ \pm 1\rangle &= \frac{1}{\sqrt{10}}\left[\sqrt{3}|5\pm 1\rangle + i\sqrt{7}|5\mp 4\rangle\right] \end{aligned} \tag{37}$$

$$\begin{aligned} |^3H\ T_2\ 0\rangle &= \frac{1}{5}\left[i\sqrt{7}|50\rangle + 3\sqrt{2}|55\rangle_+\right] \\ |^3H\ T_2\ \pm 2\rangle &= \frac{1}{\sqrt{5}}\left[-i\sqrt{2}|5\pm 2\rangle + \sqrt{3}|5\mp 3\rangle\right] \end{aligned} \tag{38}$$

$$\begin{aligned} |^3H\ V\ 0\rangle &= |55\rangle_- \\ |^3H\ V\ \pm 1\rangle &= \frac{1}{\sqrt{10}}\left[i\sqrt{7}|5\pm 1\rangle + \sqrt{3}|5\mp 4\rangle\right] \\ |^3H\ V\ \pm 2\rangle &= \frac{1}{\sqrt{5}}\left[\sqrt{3}|5\pm 2\rangle - i\sqrt{2}|5\mp 3\rangle\right] \end{aligned} \tag{39}$$

Now consider the two states $|^3P\ T_1\ 0\rangle$ and $|^3H\ T_1\ 0\rangle$. The operator X can couple them leading to the matrix of X being

$$\begin{array}{c c} & \begin{array}{cc} |^3P\ T_1\ 0\rangle & |^3H\ T_1\ 0\rangle \end{array} \\ \begin{array}{c} \langle^3P\ T_1\ 0| \\ \langle^3H\ T_1\ 0| \end{array} & \begin{bmatrix} 0 & \frac{5\sqrt{6}}{2} \\ \frac{5\sqrt{6}}{2} & \frac{25}{2} \end{bmatrix} \end{array}$$

Diagonalising the matrix yields the eigenvalues $15, -\frac{5}{2}$ with eigenvectors

$$\begin{aligned} |-\frac{5}{2}\rangle &= \frac{1}{\sqrt{7}}\left[-\sqrt{6}|^3P\ T_1\ 0\rangle + |^3H\ T_1\ 0\rangle\right] \\ |15\rangle &= \frac{1}{\sqrt{7}}\left[|^3P\ T_1\ 0\rangle + \sqrt{6}|^3H\ T_1\ 0\rangle\right] \end{aligned} \tag{40}$$

Note that the eigenvalues are exactly those obtained in our earlier diagonalisation of the $\mu = 0$ states but our description of the states is more detailed.

■ 9. Concluding Remarks

The above examples give some indication of the use of invariant operators in labelling states and constructing symmetrised states. We must next consider the states of multi-electron states arising out of configurations such as u^n and v^n. This we shall consider in the pentultimate lecture.