

Group Reduction And Its Applications To

~~Chemistry.~~ chemical Problems.

A thesis submitted for the degree of Doctor of Philosophy in the faculty of science

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Abstract.

The aim of the present thesis is to consider some aspects of the solution of problems in dimensions greater than three. In conventional treatments of problems in chemistry attention is focused on geometrical aspects i.e. the nuclear configurations of molecules and crystals. The symmetry of a system may then be described in terms of the corresponding three dimensional point and space groups. More recently, the geometry of objects in dimensions greater than three has been required in order to understand certain phenomena. This leads both to unfamiliar geometrical notions and to groups which are not encountered in the more familiar problems. An attempt has been made to lead to a treatment of these complicated higher dimensional groups in a relatively simple way.

The treatment begins with the consideration of groups in the abstract starting with those of low order and proceeding to more complicated cases. In this way both familiar and unfamiliar groups are given equal emphasis. The groups are examined in terms of operators acting on functions making a connection with the formalisms of quantum mechanics. The treatment leads to the derivation of familiar irreducible representations (and corresponding character tables) for the majority of groups.

It is possible to transform the representations to generate groups of orthogonal matrices and this makes a direct comparison with higher dimensional geometries possible. In this way examples of higher dimensional point groups are derived algebraically and their geometrical significance may be examined at a later stage.

A common application of group theory is in the classification of quantum states in terms of irreducible representations. In particular, it is customary to classify vibrational states in terms of the underlying point or space group. A complication arises for overtones of degenerate harmonic vibrations which are classifiable in terms of a much higher order symmetry group. The symmetry adaptation of the corresponding functions to the underlying point group symmetry which is restored by addition of anharmonic terms is solved using the methods developed here.

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CHAPTER ONE: INTRODUCTION.

Symmetry [1] and group theory [2, 3] are tools which are often employed to simplify the analysis in problems in chemistry. In quantum mechanics [4, 5] the symmetry of a problem is equivalent to the symmetry of the Hamiltonian operator. Identification of a group describing the symmetry leads in turn to a classification of the states of the system in terms of the irreducible representations. A striking aspect of the treatment of molecules and crystals is the importance of nuclear configuration and the symmetry often appears in the guise of the resulting geometrical structures. The corresponding point groups in molecules and space groups in crystals [6, 7] have become familiar items in the study of chemistry with a corresponding emphasis on the three dimensional nature of the objects involved. More recently, a number of phenomena have been interpreted in terms of the geometry of objects in dimensions greater than three [8, 9]. This leads both to unfamiliar geometrical notions and to groups which are not encountered in the more familiar problems. In this thesis some aspects of the solution of problems in more than three dimensions are developed.

The strategy followed is first to consider groups in the abstract [10] beginning with those of low order and proceeding to more complicated cases. In this way both familiar and unfamiliar groups are given equal emphasis. The second step is to examine these groups in terms of operators acting on functions. This makes a connection with the formalisms of quantum mechanics [11]. Indeed the procedure can be modified so that familiar irreducible representations (and corresponding character tables) can be derived for the majority of groups. In addition the representations may be expressed in

terms of orthogonal matrices [12, 13] and this makes a direct comparison with higher dimensional geometries possible. In this way examples of higher dimensional point groups are derived algebraically and their geometrical significance may then be examined.

A common application of group theory is in the classification of quantum states in terms of irreducible representations. In particular, it is customary to classify vibrational states [14, 15] in terms of the underlying point or space group. A complication arises for overtones of degenerate harmonic vibrations which are classifiable in terms of a much higher order symmetry group. The symmetry adaptation of the corresponding functions to the underlying point group symmetry which is restored by addition of anharmonic terms is solved using the methods developed here. The treatment is particularly interesting because it involves the harmonic oscillator [16, 17] and angular momentum [18, 19, 20, 21], which are the two basic models of quantum mechanics, as well as the geometrical symmetry aspects being emphasised in this thesis. In addition, it may be noted that the angular momentum is also extended to the general n -dimensional case.

CHAPTER TWO: THE SOLVABLE GROUP TREATMENT.

2.1 Introduction.

It is the purpose of the following chapter to present a method for the construction of symmetry adapted functions for solvable groups. Solvable groups [10, 22, 23, 24] are a class of groups very familiar to chemists. Most of the three dimensional point groups and all of the three dimensional space groups are solvable [25]. A solvable group is one which may be built up step by step from a cyclic subgroup. At each step a new element is added, together with its associated generating relations. The properties of the resulting augmented group are derived, including sets of symmetry adapted functions [2] which act as bases for irreducible representations. Starting from a cyclic group it is possible to construct symmetry adapted basis functions for any solvable group.

The theory of groups is generally approached in an abstract way. In the present work a connection is made between symmetry and quantum mechanics in order to introduce some familiar concepts. Quantum mechanical wavefunctions can always be written in symmetry adapted form.

2.2 Symmetry and Quantum Mechanics.

A quantum mechanical problem is defined in terms of its Hamiltonian operator. Any symmetry that the system possesses must be contained in the Hamiltonian. Symmetry itself may be described in terms of symmetry operators. A simple example is the permutation of the identifying labels of two indistinguishable particles P_{12} say. Another is the rotation or reflection of the rigid (or near rigid) nuclear framework of a molecule. Algebraically the Hamiltonian operator (H) commutes with any symmetry operator (S) associated with it i.e.

$$HS = SH \quad (2.2.1)$$

Identification of a single symmetry operator (S) of a Hamiltonian implies the existence of further operators in the sense that S may be repeated; S^2, S^3, \dots . In the case of the permutation operator already referred to, $(P_{12})^2$ can be recognised as equivalent to leaving the Hamiltonian unchanged:

$$(P_{12})^2 = E$$

where E is termed the identity operator.

In general if S is repeated N times say, it is equivalent to the identity. The set of operators $(S, S^2, \dots, S^N = E)$ is an example of a mathematical group: this particularly simple example is called a cyclic group.

In this way it can be said that a particular Hamiltonian is associated with a symmetry group: a collection of symmetry operators all of which commute with the Hamiltonian.

The group may be more complicated than the cyclic group already mentioned.

Recognition of a second symmetry operator T implies that not only powers of T itself are

symmetry operators but also any combination of powers of S and T. The complete set of such operators always constitutes a group.

In a typical quantum mechanical problem characterised by a Hamiltonian operator H, the objective is to solve the Schrödinger equation

$$H\Psi = E\Psi \quad (2.2.2)$$

Mathematically, the eigenvalues E and the corresponding eigenfunctions Ψ of the operator H are sought.

To determine the relationship of the symmetry operators S to the eigenvalues and eigenfunctions we need to consider the wave equation (2) in some detail. Frequently it is difficult if not impossible to solve the Schrödinger equation. The precise forms of the wavefunctions and the exact values of the energy are not known. In attempting to find an approximate solution, trial wave functions are often constructed. It is advantageous to choose the trial wave functions so that they are eigenfunctions of S. As a preliminary, the general properties of eigenfunctions and eigenvalues of the Hamiltonian are considered [26].

Suppose that Ψ_{j1} is found to be an eigenfunction of H with eigenvalue E_j i.e.

$$H\Psi_{j1} = E_j\Psi_{j1}$$

It is easily shown that $c\Psi_{j1}$ where c is any arbitrary number is also an eigenfunction of H with eigenvalue E_j . An infinite number of eigenfunctions have therefore been found but all are a constant times a single function.

Only one function is needed as a representative of all. It is usually chosen so that

$$\int \Psi_{j1}^* \Psi_{j1} d\tau = 1$$

Then Ψ_{j1} is said to be normalised.

A useful geometrical analogy [27] is to represent this result as a one-dimensional space: i.e. a straight line. Then, every point on the line has a coordinate c and represents one of the functions $c\Psi_{j1}$. The function Ψ_{j1} itself has $c = 1$ and acts as a unit vector or basis vector for the space.

Suppose that Ψ_{j2} is found to be an eigenfunction of H with eigenvalue E_j and

$$\Psi_{j2} \neq c\Psi_{j1}$$

In such cases the eigenvalue E_j is said to be degenerate and not only are the initial set of eigenfunctions solutions of the wave equation, but any linear combination of them is also a solution giving the same eigenvalue. Thus

$$(c\Psi_{j1} + d\Psi_{j2})$$

in which c and d are two arbitrary constants, are also eigenfunctions with eigenvalue E_j .

The energy level E_j is then said to be two-fold degenerate since two functions are required to describe all the associated solutions.

In the geometrical analogy already introduced a two-dimensional space is required. c and d are coordinates and Ψ_{j1} and Ψ_{j2} are basis vectors. Any two functions may be chosen provided they are not linearly related. It is most convenient to choose them so that they are both normalised and mutually orthogonal i.e.

$$\int \Psi_{j1}^* \Psi_{j2} d\tau = 0$$

This corresponds to use of Cartesian coordinates and basis vectors in the function space.

Extension to higher degeneracies follows in a natural way.

A general property of eigenfunctions of a Hamiltonian is that they are necessarily orthogonal if they belong to different eigenvalues.

Now the complete set of eigenfunctions can be chosen so that they are normalised and functions within a degenerate set are orthogonal. Summarising

$$\int \Psi_{jp}^* \Psi_{kq} d\tau = \delta_{jk} \delta_{pq} \quad (2.2.3)$$

The effect of symmetry operators on eigenfunctions may now be considered. The key consideration is that application of a symmetry operator to an eigenfunction cannot make any observable difference to the system. In this way, the energy cannot be altered and the resulting function must be an eigenfunction with the same energy value i.e. it can be represented as a linear combination of the basis functions.

$$S\Psi_p = \sum_{q=1}^k c_{qp}(S) \Psi_q \quad p = 1, 2, \dots, k \quad (2.2.4)$$

(The energy level label j has been omitted for convenience but it is assumed that the energy is k -fold degenerate).

It is seen that the effect of the symmetry operator on Ψ_p is to generate a matrix $C(S)$ with elements $c_{qp}(S)$.

Consider now the effect of two symmetry operators S and T . The result must itself be equivalent to a single symmetry operator U where

$$U = TS$$

then

$$\begin{aligned}
U\Psi_p &= \sum_{m=1}^k c_{mp}(U)\Psi_m \\
&= TS\Psi_p \\
&= T\left\{ \sum_{q=1}^k c_{qp}(S)\Psi_q \right\} \\
&= \sum_{m=1}^k c_{mq}(T) \sum_{q=1}^k c_{qp}(S)\Psi_m
\end{aligned}$$

equating coefficients of Ψ_m

$$c_{mp}(U) = \sum_{q=1}^k c_{mq}(T)c_{qp}(S) \quad (2.2.5)$$

which is equivalent to saying that the matrix $C(U)$ is the matrix product of $C(S)$ and $C(T)$ i.e.

$$C(U) = C(T)C(S)$$

In the language of group theory, the set of matrices $C(S)$, one for each member of the group, forms a (matrix) representation of the group. The matrices are generated by considering the effect of the symmetry operators on the eigenfunctions. The functions themselves (Ψ_q) are said to form a basis for the representation. It may also be noted that if the complete symmetry group of the Hamiltonian is considered, then the representation is irreducible. The exact significance of irreducible representations will become apparent in the following text.

It is recalled that the more usual situation is that the exact solution to a problem is not known and that trial approximate functions are sought. Trial functions are consistent with

the symmetry if they form bases for irreducible representations of the corresponding group.

Such functions are frequently called symmetry adapted functions and in the following sections a method for the construction of symmetry adapted functions for finite solvable groups will be developed.

In order to introduce the effect of symmetry on a problem the effect of individual symmetry operators is considered successively. If it is assumed that a given symmetry operator A is equivalent to the identity after a finite number of steps then the first stage is equivalent to considering a cyclic group.

2.3 Symmetry reduction for a single finite order operator:

The cyclic group.

In this section, the treatment for a general finite order symmetry operator A is developed.

It is supposed that

$$A^M = E \quad (2.3.1)$$

The eigenvalues of A can be determined as follows. Suppose an eigenvalue E_j and a corresponding eigenfunction Ψ_j have been identified.

$$A\Psi_j = E_j\Psi_j$$

Then Ψ_j remains an eigenfunction of all powers of A with eigenvalues the corresponding powers of E_j .

$$A^2\Psi_j = E_j(A\Psi_j) = E_j^2\Psi_j$$

...

$$A^M\Psi_j = E_j^M\Psi_j$$

But the last operator is the identity which leaves a function unchanged so that any eigenvalue of A satisfies

$$E_j^M = 1 \quad (2.3.2)$$

i.e. there are M distinct eigenvalues of A , these being the M^{th} roots of unity. These take the form

$$\begin{aligned} \varepsilon_M^p &= \exp\left(\frac{2\pi ip}{M}\right) \\ &= \cos\left(\frac{2\pi p}{M}\right) + i \sin\left(\frac{2\pi p}{M}\right) \end{aligned} \quad (2.3.3)$$

The functions are cyclical and the range of p which gives the M distinct roots can be chosen as convenient. For example

$$p = 0, 1, 2, \dots, M-1$$

emphasises that integer arithmetic in p is to be taken modulo M whereas

$$p = 0, \pm 1, \pm 2, \dots$$

emphasises the result that plus and minus values of an integer correspond to complex conjugates i.e.

$$\varepsilon_M^p = \varepsilon_M^{-p} \quad (2.3.4)$$

It is interesting to note that the eigenvalues of A have been found without knowledge of the corresponding eigenfunctions. In order to determine the form of the eigenfunctions of A we begin by considering an arbitrary function θ_0 . Then the effect of A is to generate a second function θ_1 :

$$A\theta_0 = \theta_1$$

Successive powers of A generate new functions, the set so generated being eventually terminated by the finite power of A .

$$A\theta_0 = \theta_1$$

$$A^2\theta_0 = \theta_2 \quad (2.3.5)$$

...

$$A^M\theta_0 = \theta_0$$

In this way, the effect of a symmetry operator A on an arbitrary function is to generate a set of M functions

$$\theta_0 \ \theta_1 \ \theta_2 \ \dots \ \theta_{M-1}$$

The objective now is to take linear combinations of the above functions of the form

$$\sum_m c_m \theta_m$$

in such a way as to generate eigenfunctions of A i.e.

$$A \left[\sum_m c_m \theta_m \right] = \varepsilon_M^p \left[\sum_m c_m \theta_m \right] \quad (2.3.6)$$

The coefficients c_m are readily found (see appendix 2.1) and eigenfunctions of A may then be written

$$\Psi_p = N \sum_{m=0}^{M-1} \exp\left(\frac{-2\pi i p m}{M}\right) \theta_m \quad (2.3.7)$$

The factor N is a normalisation constant and emphasises that multiplication by a constant still leaves an eigenfunction and to act as a reminder that in practical applications the function would usually be normalised.

It is important to note here that the symmetry operator A has complex eigenvalues which implies that the operator is not Hermitian. However, it can be shown (see appendix 2.2) that the eigenfunctions of A are orthogonal i.e.

$$\int \Psi_j^* \Psi_k d\tau = \delta_{jk} \quad (2.3.8)$$

The procedure described in this section shows how eigenfunctions of A can be constructed from any arbitrary function. The resulting functions are divided into sets each labeled by one of the eigenvalues p of A.

It might be recognised that the treatment developed in this section exactly parallels a description in terms of group theory. The terminology of symmetry operators has been

used and attention confined to a very simple case. It is useful for the further development of this work to recast the results in the language of group theory.

The set of operators A and its powers is recognised as a group of order M . It is an Abelian group since all its operators commute and a cyclic group because all operators are powers of a single operator A . Equation (1)

$$A^M = E$$

is the generating relation of the group.

The set of functions

$$\theta_0 \ \theta_1 \ \theta_2 \ \dots \ \theta_{M-1}$$

generated from an arbitrary function by A and its powers (5) form a basis for a representation of dimension M of the group. By transforming to the new functions Ψ_p , defined in (7), the set is decoupled with respect to the group. Each is an eigenfunction of A and its powers and in general

$$A^m \Psi_p = \varepsilon_M^{mp} \Psi_p \quad (2.3.9)$$

The single function Ψ_p is then said to form a basis for a representation of order 1: an irreducible representation.

The procedure has thus transformed the original reducible representation of dimension M into M irreducible representations of order one. Since the original function θ_0 is arbitrary, it is always possible to make the reduction in this way and all possible irreducible function types (i.e. all possible irreducible representations) have been found.

The set Ψ_p are also called symmetry adapted functions. Combining (7) and (5)

$$\Psi_p = \sum_{m=0}^{M-1} \exp\left(\frac{-2\pi i p m}{M}\right) A^m \theta_0 \quad (2.3.10)$$

The symmetry adapted function can then be regarded as being derived by the action of a projection operator [28] on the arbitrary function.

The characters of the irreducible representations may be recognised as the factors ε appearing in (2.3.9). In the case considered here where only one dimensional irreducible representations are involved this factor can equivalently be interpreted as the eigenvalue, the (single) matrix element or the character.

The character table [29] for the cyclic group C_M may thus be written in a very compact form.

C_M	A^m	$m = 0, 1, \dots M-1$
Γ_p	ε_M^{mp}	$p = 0, 1, \dots M-1$

In the conventional treatment of applications to group theory in chemistry, three properties of irreducible representations are quoted:

1. The number of irreducible representations is equal to the number of classes.

In a cyclic group each element is in a class by itself. It is seen that the number of irreducible representations is equal to the order of the group and hence to the number of classes.

2. The sum of the squares of the dimensions of the irreducible representations is equal to the order of the group.

This result is clearly satisfied in this example.

3. Different irreducible representations λ and μ are orthogonal in the sense that their characters χ satisfy

$$\sum_A \chi^\lambda(A) \chi^\mu(A) = \delta_{\lambda\mu} g \quad (2.3.11)$$

where the sum runs over the elements A of the group of order g .

It can be proved that

$$\sum_{m=0}^{M-1} \varepsilon_M^{pm} \varepsilon_M^{qm} = \delta_{pq} g \quad (2.3.12)$$

this being the analogous expression for a cyclic group.

In conclusion it is reemphasised that the treatment does not use group theory but that in effect derives the properties of a cyclic group from first principles. The latter remarks in this section merely demonstrate that the results of the present development can be translated into the terminology of group theory.

2.4 Symmetry reduction for commuting finite operators:

Abelian groups.

The treatment of the previous section is readily extended to take account of a second finite order operator which commutes with the first. To the expression

$$A^M = E \quad (2.4.1)$$

is added

$$B^N = E \quad (2.4.2)$$

with the cross relation

$$AB = BA \quad (2.4.3)$$

Functions adapted to the symmetry described by A may be generated from an arbitrary function by the methods of the previous section. Using the projection operator form (2.3.10)

$$\Psi_{po} = N \sum_m \exp\left(\frac{-2\pi i p m}{M}\right) \theta_{mo} \quad (2.4.4)$$

The sequence of equations

$$A(B\Psi_{po}) = BA\Psi_{po} = \varepsilon_M^p (B\Psi_{po}) \quad (2.4.5)$$

shows that the functions generated from Ψ_{po} by B (and its powers) remain eigenfunctions of A with the same eigenvalue. This key result arises because the operators commute. It is then possible to construct functions symmetry adapted with respect to B without losing the simplification already achieved with respect to A.

$$\begin{aligned}
\Psi_{pq} &= N \sum_n \varepsilon_N^{nq*} B^n \Psi_{p0} \\
&= N \sum_m \sum_n \varepsilon_M^{pm*} \varepsilon_N^{nq*} A^m B^n \theta_{00} \\
&= N \sum_m \sum_n \varepsilon_M^{pm*} \varepsilon_N^{qn*} \theta_{mn}
\end{aligned} \tag{2.4.6}$$

The last form of the equation connects with (2.3.7) for a single operator and gives a generalisation of (2.3.5):

$$A^m B^n \theta_{00} = \theta_{mn} \tag{2.4.7}$$

In summary, the method of symmetry reduction applied to a single finite order operator may be used for a second provided the two operators commute. This parallels the result in quantum mechanics that it is always possible to construct simultaneous eigenfunctions of two commuting operators. Clearly the procedure may be repeated indefinitely provided each new operator commutes with all those that have gone before.

As was done in the previous section the results, which have been derived without using the methods of group theory, may be recast in the language of group theory.

The operators A , B and their powers form a group of order MN . It is an Abelian group since all group elements commute. Equations (1) to (3) are generating relations of the group. The group is not itself cyclic but it is the direct product of two cyclic groups indicated by the notation $C_M \times C_N$.

The irreducible representations of the group are all one-dimensional and a condensed character table analogous to table one can be constructed.

$C_M \times C_N$	$A^m B^n$	$p, m = 0, 1, \dots, M-1$
Γ_{pq}	$\varepsilon_M^{pm} \varepsilon_N^{qn}$	$q, n = 0, 1, \dots, N-1$

The extension to further commuting operators is straightforward: each leads to a new factor in the character which is a root of unity, a new index in the specification of the irreducible representation and an extension of the direct product.

It is possible to show that all Abelian groups can be expressed in the form of direct products of cyclic groups so that the treatment given in this section applies to all Abelian groups.

2.5 Symmetry reduction for non-commuting finite operators.

Dihedral groups.

If a problem has symmetry described by two or more non-commuting operators, progress is still possible in certain cases. To make the considerations involved more clear, attention is first directed towards one particular example.

A first symmetry operator satisfies

$$A^3 = E \quad (2.5.1)$$

and a second

$$B^2 = E \quad (2.5.2)$$

The two do not commute but are related by

$$AB = BA^2 \quad (2.5.3)$$

The equations are given in abstract form but may be recognised as equivalent to the familiar point group C_{3v} .

Functions which are symmetry adapted to A are readily constructed using the methods of previous sections.

$$\Psi_0 = \theta_0 + \theta_1 + \theta_2$$

$$\Psi_1 = \theta_0 + \varepsilon_3^1 \theta_1 + \varepsilon_3^{1*} \theta_2 \quad (2.5.4)$$

$$\Psi_2 = \theta_0 + \varepsilon_3^{1*} \theta_1 + \varepsilon_3^1 \theta_2.$$

It is noted that the simplification made here with respect to A can always be used irrespective of whether it is possible to make a further simplification with respect to B or indeed any other symmetry operator involved in a problem.

Now the effect of the second operator on the functions (4) will be examined.

The sequence of equations

$$A(B\Psi_p) = BA^2\Psi_p = \varepsilon_3^{2p}(B\Psi_p) \quad (2.5.5)$$

shows that the new function $(B\Psi_p)$ is still an eigenfunction of A but that the eigenvalue now corresponds to $2p$. Symbolically

$$B\Psi_p = \phi_{2p} \quad (2.5.6)$$

Remembering that all integers are to be taken modulo 3, the following table can be constructed.

p	$2p \pmod{3}$
0	0
1	$2 \equiv 1^*$
$2 \equiv 1^*$	1

Two cases may be distinguished. When $p = 0$, the new function (6) generated by B remains an eigenfunction of A with the same eigenvalue. For this special value, B behaves as if it commutes with A and simultaneous eigenfunctions may be constructed.

$$\Phi_{00} = (\Psi_0 + \varepsilon_2^0 \phi_0) = (\Psi_0 + \phi_0)$$

$$\Phi_{01} = (\Psi_0 + \varepsilon_2^1 \phi_0) = (\Psi_0 - \phi_0) \quad (2.5.7)$$

On the other hand, functions of types 1 and 2 (or types 1 and 1^* to emphasise that the representations though not necessarily the functions are complex conjugates) are interchanged by the action of B .

$$B\Psi_1 = \phi_2$$

$$B\phi_2 = \Psi_1 \quad (2.5.8)$$

The pair of functions are eigenfunctions of A but not eigenfunctions of B . They may be transformed into eigenfunctions of B using the methods of section 2.

$$B(\Psi_1 + \phi_2) = +1(\Psi_1 + \phi_2)$$

$$B(\Psi_1 - \phi_2) = -1(\Psi_1 - \phi_2) \quad (2.5.9)$$

The new pair of functions are eigenfunctions of B but not eigenfunctions of A. It is thus impossible to construct functions which are simultaneously eigenfunctions of A and B. As the problem has both symmetries, there must be a double degeneracy to allow both possibilities.

It has therefore been shown that starting from an arbitrary function there are only three types of symmetry adapted function possible. Two of the types are non-degenerate and correspond to simultaneous eigenfunctions of A and B with pairs of eigenvalues labelled by (0,0) and (0,1). The third type is doubly degenerate and may be labelled by a pair of eigenvalues of A: 1 and 1*.

It may be noted that starting from an arbitrary function, there are two pairs of degenerate functions, the second being Ψ_2 and ϕ_1 . This draws attention to two points. The discussion so far has always been based on the general case where each symmetry operator acting on the arbitrary function generates a new function so that the number of functions generated is equal to the order of the group i.e. six in the present example.

If the arbitrary function is already partially or wholly symmetry adapted, then the number of functions is actually less than the order of the group. This does not have to be allowed for explicitly in the projection operator formalism because null functions are automatically generated for the missing members of the set.

The second point is that, in contrast to the case of commuting operators, the symmetry reduction is not complete with respect to the set generated from an arbitrary function which gives the maximum possible number of distinct functions. Whereas only one function of each non-degenerate type is generated, there are two pairs of doubly degenerate functions.

As with the previous two analyses, all the symmetry properties of interest in the present context have been developed in terms of symmetry operators and their effect on representative functions. The methods of group theory have not been used directly.

The present results are now re-expressed in the language of group theory.

The basic operator relations (1) to (3) generate a group of order six and may be used to form the multiplication table of all pair products. They may in turn be used to evaluate the order of each group member and to identify the inverse of each.

Element (S):	E	A	A ²	B	AB	A ² B
Order of S:	1	3	3	2	2	2
Inverse (S ⁻¹):	E	A ²	A	B	AB	A ² B

It is recalled that elements S and T are conjugate if there is a third member of the group U such that

$$USU^{-1} = T \quad (2.5.10)$$

or equivalently

$$US = TU. \quad (2.5.11)$$

Then sets of all conjugate elements within a group are called classes. For the group under consideration here, there are three classes:

1. E

2. A A² (2.5.12)

3. B AB A²B

Elements within one class always have the same order but the converse is not in general true.

The non-degenerate symmetry adapted functions introduce no new concepts, but the two-fold degenerate case is now discussed in some detail. Taking one of the pairs of degenerate functions, operator equations may be written for all group members

$$\begin{aligned}
 E\Psi_1 &= \Psi_1 & E\phi_2 &= \phi_2 \\
 A\Psi_1 &= \varepsilon_3^1 \Psi_1 & A\phi_2 &= \varepsilon_3^{1*} \phi_2 \\
 A^2\Psi_1 &= \varepsilon_3^{1*} \Psi_1 & A^2\phi_2 &= \varepsilon_3^1 \phi_2 \\
 B\Psi_1 &= \phi_2 & B\phi_2 &= \Psi_1 \\
 AB\Psi_1 &= \varepsilon_3^{1*} \phi_2 & AB\phi_2 &= \varepsilon_3^1 \Psi_1 \\
 A^2B\Psi_1 &= \varepsilon_3^1 \phi_2 & A^2B\phi_2 &= \varepsilon_3^{1*} \Psi_1
 \end{aligned} \tag{2.5.13}$$

The characters of the associated irreducible representations may be found directly from these equations by summing the diagonal coefficients. Then noticing that

$$1 + \varepsilon_3^1 + \varepsilon_3^{1*} = 0$$

the characters are

Element (S):	E	A	A ²	B	AB	A ² B
Character of S:	2	-1	-1	0	0	0

These are consistent with the general result that all elements in the same class have the same character. The full character table for all three irreducible representations may be written in a familiar form.

D ₃	E	2A	3B
$\Gamma(\Phi_{00})$	1	1	1
$\Gamma(\Phi_{01})$	1	1	-1
$\Gamma(\Psi_1, \phi_2)$	2	-1	0

In the familiar Schönflies notation, the representations would be denoted by A₁, A₂ and E respectively.

No direct reference has so far been made to matrices and the operator equations actually contain all the necessary information and can be used without further modification. However, matrices are more familiar in chemical applications and will be useful for some aspects of this work.

A general connection may be made as follows. For a set of n functions which form a basis for a representation of a group, the effect of a group element S may be written

$$S\Psi_p = \sum_{q=1}^n c_{qp}(S)\Psi_q \quad (2.2.4)$$

Then if for example three elements of the group are related by

$$U = TS$$

it has been shown that

$$c_{mp}(U) = \sum_{q=1}^n c_{mq}(T)c_{qp}(S) \quad (2.2.5)$$

The matrices defined in this way form a (matrix) representation of the group. Applying this to the doubly degenerate representation, the following matrices are:

$$\begin{array}{ccc}
 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} \varepsilon_3^1 & 0 \\ 0 & \varepsilon_3^{1*} \end{pmatrix} & \begin{pmatrix} \varepsilon_3^{1*} & 0 \\ 0 & \varepsilon_3^1 \end{pmatrix} \\
 E & A & A^2 \\
 \\
 \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} & \begin{pmatrix} 0 & \varepsilon_3^1 \\ \varepsilon_3^{1*} & 0 \end{pmatrix} & \begin{pmatrix} 0 & \varepsilon_3^{1*} \\ \varepsilon_3^1 & 0 \end{pmatrix} \\
 B & AB & A^2B
 \end{array}$$

The representation can be more compactly written by specifying only the matrices corresponding to the generators A and B and then using the generating relations when more detail is needed.

It is also noted in this example that the matrices are different for each group member.

This is termed a faithful representation of the group. The set of matrices themselves form a matrix group (under matrix multiplication).

The group developed in this section is sometimes called the dihedral group D_3 . The treatment can be applied directly to all dihedral groups D_n defined by the relations

$$A^M = B^2 = E \quad AB = BA^{M-1}.$$

2.6 Symmetry reduction for non-commuting finite operators:

Solvable groups.

In the last section symmetry reduction was effected for a particular dihedral group. The method consisted of solving the problem for a subgroup (in this case the cyclic group based on powers of A) and then examining the effect of adding a second operator B which augments the subgroup to give the full dihedral group.

The generalised procedure will consist in progressing to larger and larger groups at each step adding one new operator.

The question can be asked: what is the relationship between the subgroup and group which makes it possible to solve the problem in this way? Before the question can be answered, some more detailed concepts in group theory must be developed [10].

To classify groups in more detail, it is useful to introduce subgroups. A subgroup (S) of a group (G) is a subset of elements which constitute a group. The order of the subgroup (s) is always an integral factor of the order of the parent group (g) i.e. $g/s = n$ where n is called the index of S in G. The group G may be written as a series in terms of its subgroup in two ways:

$$G = SE + SR_2 + \dots + SR_n$$

$$G = ES + S_2S + \dots + S_nS \quad (2.6.1)$$

These are respectively referred to as the expansion of G into right or left-handed cosets relative to S. The subsets SE, SR_2 , ..., SR_n have no elements in common and each contain

s distinct elements. The choice of elements E, R_2, \dots, R_n is not unique. They are called coset representatives. Only the first member SE is a group.

Since group multiplication is not in general commutative, it is not expected that the right and left handed cosets will be the same. A subgroup for which they are the same is called an invariant subgroup. The concept of an invariant subgroup is of central importance in the present context and follows from the concept of invariant elements. Two group elements A and B are said to be conjugate if there is a third element T such that

$$TAT^{-1} = B$$

or

$$TA = BT \tag{2.6.2}$$

A group may be divided into sets of conjugate elements, each such set is said to form a class.

An element which is conjugate with itself and no other element is called a self-conjugate or invariant element of the group to which it belongs. In an Abelian group every element is invariant and hence each element is in a class by itself.

Similarly, two subgroups S and R are said to be conjugate if there is a group element T such that

$$TST^{-1} = R$$

or

$$TS = RT \tag{2.6.3}$$

The second form implies that for two conjugate subgroups the right handed cosets of one group are the same as the left handed cosets of the other.

If a subgroup has no other conjugate subgroups, it is called a self-conjugate subgroup.

Then the left and right handed cosets are the same and the subgroup is also an invariant subgroup.

If the element A belongs to an invariant subgroup, so does every element of the form TAT^{-1} where T is any element of \mathbb{G} i.e. each element of the class of A is contained in the subgroup. Hence, an invariant subgroup contains whole classes of the parent group.

The important properties of an invariant subgroup may be summarised.

1. It is a self conjugate subgroup.
2. Its right and left handed cosets are identical.
3. It contains whole classes of the parent group.

Based on the concept of the invariant subgroup, groups in general may be divided into two kinds: simple groups which have no invariant subgroups and composite groups.

Cyclic groups of prime order are simple, other Abelian groups are composite. There are non-Abelian simple groups. The smallest of them is of order 60 and corresponds to the rotations of a regular icosahedron (point group I) or equivalently the even permutations of 5 indistinguishable objects (the alternating group A_5). In fact, all higher alternating groups are simple.

Returning to invariant subgroups, there is a complementary concept which is also important. If a group is expanded as in (1) relative to an invariant subgroup S , then the set of n distinct cosets SE, SR_2, \dots, SR_n form a group under coset multiplication. This is called the factor (or quotient) group of S in \mathbb{G} and is denoted by \mathbb{G}/S . Its order is g/s . If \mathbb{G}/S is of prime order then S is called a maximum invariant subgroup.

If a finite group \mathfrak{G} may be expressed as a series of groups:

$$\mathfrak{G}, \mathfrak{S}_1, \mathfrak{S}_2, \dots, \mathfrak{S}_p \equiv C_1$$

such that each group is a maximum invariant subgroup of the previous one, then the group is said to be solvable. Such a series is called a composition series. The corresponding factor groups $\mathfrak{G}/\mathfrak{S}_1, \mathfrak{S}_1/\mathfrak{S}_2 \dots$ are all of prime order and are therefore necessarily cyclic.

All three-dimensional point groups (except the icosahedral groups) are solvable. Thus, the group D_3 has the following composition series

$$D_3 ; C_3 ; C_1$$

and the corresponding composition indices are

$$(2) (3)$$

As a second example, using point group notation

$$T ; D_2 ; C_2 ; C_1$$

$$(3) (2) (2)$$

In the context of abstract group theory, the solvable group is useful because it provides a means of building up the structure of a group step by step.

It is now possible to show how symmetry adapted functions may be constructed for any solvable group [25]. Since the composition indices are all prime, it is evident that the last but one member of the composition series must be a cyclic group. The treatment in section three shows how symmetry adapted functions of cyclic groups may be constructed and classified. An induction argument may then be followed. It is supposed that a set of symmetry adapted functions have been found for a particular (not necessarily cyclic)

member of the composition series. Then it will be shown that those for the next higher member can be formed.

The higher group (\mathfrak{G}) may be expanded in terms of cosets of the lower group (\mathfrak{L}), it being supposed that the corresponding index is j .

$$\mathfrak{G} = \mathfrak{L}E + \mathfrak{L}P + \mathfrak{L}P^2 + \dots + \mathfrak{L}P^{j-1} \quad (2.6.4)$$

Since the factor group is cyclic, it will always be possible to find coset representatives which are powers of a single element P . It is recalled that the right and left hand cosets are the same for an invariant subgroup.

There are two possible ways in which an element of \mathfrak{L} may behave with respect to the augmenting element P .

(1) It commutes with P, P^2, \dots

(2) It generates a cycle of j different group elements;

$$B_1P = PB_2 \quad B_2P = PB_3 \quad \dots$$

which implies

$$B_1P^2 = P^2B_3 \quad B_2P^2 = P^2B_4 \quad \dots$$

$$B_1P^j = P^jB_1 \quad \dots$$

Since j is prime, there are no intermediate possibilities.

The group may then be written in the order

$$\mathfrak{L}: \quad E; A; \dots; B_1, B_2, \dots; C_1, C_2, \dots; \dots$$

i.e. first the commuting elements and second the cycles of elements of type (2).

A right coset then has elements

$$\mathfrak{L}P: \quad EP; AP; \dots; B_1P, B_2P, \dots, B_jP; C_1P, C_2P, \dots, C_jP;$$

and the left coset is identically ordered if it is written

$$PL: PE; PA; \dots; PB_2, PB_3, \dots, PB_1; PC_2, PC_3, \dots, PC_1;$$

It is assumed that the symmetry adapted functions of \mathbf{L} have already been constructed.

They will be divisible into subsets, each belonging to an irreducible representation λ_1 of \mathbf{L} .

A typical function is denoted by $\Psi_m^{\lambda_1}$. Then the effect of D an element of \mathbf{L} on the function

has the form

$$D\Psi_m^{\lambda_1} = \sum_n c_{nm}^{\lambda_1}(D)\Psi_n^{\lambda_1} \quad (2.6.5)$$

The coefficients c forming the representation matrix. The higher group \mathfrak{G} is obtained by

adding P and its powers up to $(j-1)$. The effect of P on the symmetry adapted functions of

\mathbf{L} can be deduced by considering a typical element of type (1) and of type (2).

$$AP\Psi_m^{\lambda_1} = PA\Psi_m^{\lambda_1} = \sum_n c_{nm}^{(\lambda_1)}(A)P\Psi_n^{\lambda_1} \quad (2.6.6)$$

since A and P commute. For type (2), the situation is more complicated.

$$B_1 P\Psi_m^{\lambda_1} = PB_2 \Psi_m^{\lambda_1} = \sum_n c_{nm}^{(\lambda_1)}(B_2)P\Psi_n^{\lambda_1} \quad (2.6.7)$$

The effect is that the matrix which was allocated to B_2 is now allocated to B_1 . This is a

potentially different representation which will be labeled λ_2 . In this way (7) becomes

$$B_1 P\Psi_m^{\lambda_1} = PB_2 \Psi_m^{\lambda_1} = \sum_n c_{nm}^{(\lambda_2)}(B_1)P\Psi_n^{\lambda_1} \quad (2.6.8)$$

The net result is that under P, P^2, \dots, P^j , irreducible representation of \mathbf{L} labeled by $\lambda_1 \lambda_2 \dots$

λ_j are generated. Since j is a prime number, there are only two distinct possibilities.

(1) The representations are all equivalent.

(2) They are all different.

In the first case, the symmetry behavior with respect to \mathbf{L} is fully maintained on augmentation to \mathbf{G} and the functions may be combined to give eigenfunctions of P :

$$\Psi_{m\mu}^{\lambda_1} = N \sum_{k=0}^{j-1} \epsilon_j^{k\mu} P^k \Psi_m^{\lambda_1} \quad \mu = 0, 1, \dots, j-1. \quad (2.6.9)$$

The degeneracy of the new irreducible representations of \mathbf{G} is the same as that of the representation of \mathbf{L} from which it is derived.

In the second case, P generates different representations of \mathbf{L} so that it is not possible to construct simultaneous eigenfunctions. The total set of functions

$$\Psi_m^{\lambda_1}, P \Psi_m^{\lambda_1}, P^2 \Psi_m^{\lambda_1}, \dots, P^{j-1} \Psi_m^{\lambda_1} \quad (2.6.10)$$

span a new representation of degeneracy j times higher than the representation from which it is derived.

The treatment developed so far is complete in two respects. First the generating relationships can be used to obtain full details of the abstract group: multiplication table, class structure and subgroup relationships. Second the manipulations of a representative function space enable the irreducible representations to be specified, the character table to be drawn up and explicit forms of matrices corresponding to each irreducible representation to be deduced. It can be noted that the matrices which arise directly are unitary. They are often monomial [12, 25, 31, 32] or "pseudo-permutation" matrices i.e. there is only one non zero element in any given row or column and the non zero elements are all roots of unity.

The following examples will illustrate the method further and will also provide material for use in applications. Some of the groups to be treated may be unfamiliar in the sense that they do not correspond to any of the three dimensional point groups.

2.7 Examples.

2.7.1. The Quaternion Group and a generalisation to the bicyclic groups.

The quaternion group [33, 34] is the lowest order group which does not correspond to a three dimensional point group. It may be constructed by adding to $A^4=E$ an element B such that

$$B^2 = A^2 \quad AB = BA^3 \quad (2.7.1)$$

Let Ψ_p be an eigenfunction of A and its powers

$$A^m \Psi_p = \varepsilon_4^{pm} \Psi_p \quad p = 0, \pm 1, 2.$$

Addition of B yields the following

$$AB \Psi_p = BA^3 \Psi_p = \varepsilon_4^{3p} B \Psi_p$$

and therefore

$$B \Psi_p = \Phi_{3p}$$

Then it should be noted that

$$B \Phi_{3p} = B^2 \Psi_p = A^2 \Psi_p = \varepsilon_4^{2p} \Psi_p$$

Thus the two basic interchange equations are

$$\begin{aligned} B \Psi_p &= \Phi_{3p} \\ B \Phi_{3p} &= \varepsilon_2^p \Psi_p \end{aligned} \quad (2.7.2)$$

When $p = 0$, $p \equiv 3p$ and $\varepsilon_2^p = 1$, so that simultaneous eigenfunctions of B may be constructed.

$$\Psi_{0k} = \Psi_0 + \varepsilon_2^{-k} \Phi_0 \quad k = 0, 1.$$

Similarly when $p = 2$, $p \equiv 3p$ and $\varepsilon_2^p = 1$ and the symmetry adapted functions have the same form

$$\Psi_{2k} = \Psi_2 + \varepsilon_2^{-k} \Phi_2$$

When $p = 1$ $3p \equiv -1$, and a doubly degenerate representation is formed

$$B\Psi_1 = \Phi_{-1}$$

$$B\Phi_{-1} = -\Psi_1$$

The information given allows all possible properties of the group to be deduced for example, orders of the elements and their class structure.

Class		Order
E		1
A^2		2
A	A^3	4
B	A^2B	4
AB	A^3B	4

The character table is also readily written

Q_4	E	A^2	2A	2B	2AB
Γ_{00}	1	1	1	1	1
Γ_{01}	1	1	1	-1	-1
Γ_{20}	1	1	-1	1	-1
Γ_{21}	1	1	-1	-1	1
$\Gamma_{(1,-1)}$	2	-2	0	0	0

From (2.5.14) and (2.5.15) matrix representations can be constructed. The two dimensional matrices are as follows

$$\begin{array}{cccc} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} & \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} & \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} \\ E & A & A^2 & A^3 \\ \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix} & \begin{pmatrix} 0 & -i \\ -i & 0 \end{pmatrix} & \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix} & \begin{pmatrix} 0 & i \\ i & 0 \end{pmatrix} \\ B & AB & A^2B & A^3B \end{array}$$

The fourth roots have been given their explicit values $1, i, -1, -i$.

This group is usually called the Quaternion group and is denoted by Q . The set of quaternions $1, i, j, k$ combine according to the following rules

$$i^2 = j^2 = k^2 = -1$$

$$ij = k \quad ji = -k$$

$$jk = i \text{ etc.}$$

The set of eight elements $\pm 1, \pm i, \pm j, \pm k$ forms a group with the abstract form just discussed.

The bicyclic groups.

The quaternion group is the first member of a series: the bicyclic groups [35]. None of them correspond to three dimensional point groups. They have the general form

$$Q_n: \quad A^n = E \quad B^2 = A^{n/2} \quad AB = BA^{n-1} \quad (2.7.3)$$

The next member Q_6 is subtly different from Q and is now analysed.

$$Q_6: \quad A^6 = E \quad B^2 = A^3 \quad AB = BA^5 \quad (2.7.4)$$

As before eigenfunctions of A are written Ψ_p and satisfy

$$A^m \Psi_p = \varepsilon_6^{pm} \Psi_p \quad p = 0, \pm 1, \pm 2, 3$$

and the analogues to (2) are

$$\begin{aligned} B\Psi_p &= \Phi_{5p} \\ B\Phi_{5p} &= \varepsilon_2^p \Psi_p \end{aligned} \quad (2.7.5)$$

When $p = 0$, the analysis again parallels the Q group leading to simultaneous eigenfunctions

$$\Psi_{0k} = \Psi_0 + \varepsilon_2^{-k} \Phi_0$$

However when $p = 3$, $p \equiv 5p$ but $\varepsilon_2^p = -1$ and the basic equations become

$$B\Psi_3 = \Phi_3$$

$$B\Phi_3 = -\Psi_3$$

Since $B^2 = A^3$, both Ψ_3 and Φ_3 are eigenfunctions of B^2 with eigenvalue -1 and so combinations of the two which are eigenfunctions of B must have eigenvalues i and $-i$ (or ε_4^1 and ε_4^{-1}).

Combinations are then readily shown to be

$$\Psi_{3k} = \Psi_3 + \varepsilon_4^{-k} \Phi_3 \quad k = 1, -1$$

A composite notation may be developed by replacing k by $2k$ in the $p = 0$ functions

$$\Psi_{pk} = \Psi_p + \varepsilon_4^{-k} \Phi_p \quad pk = 00, 02, 31, 3-1$$

Doubly degenerate representations result for $p = 1, -1$ and $2, -2$.

$$B\Psi_1 = \Phi_{-1}$$

$$B\Phi_{-1} = -\Psi_1$$

$$B\Psi_2 = \Phi_{-2}$$

$$B\Phi_{-2} = \Psi_2$$

Again, orders and classes may be determined.

Class	Order
E	1
A^3	2
A A^5	6
A^2 A^4	3
B A^2B A^4B	4
AB A^3B A^5B	4

and the character table is

Q_6	E	A^3	2A	$2A^2$	3B	3AB
Γ_{00}	1	1	1	1	1	1
Γ_{02}	1	1	1	1	-1	-1
Γ_{31}	1	-1	-1	1	i	$-i$
Γ_{3-1}	1	-1	-1	1	$-i$	i
$\Gamma_{(1,-1)}$	2	-2	1	-1	0	0
$\Gamma_{(2,-2)}$	2	2	-1	-1	0	0

2.7.2 The alternating group A_4 .

The group A_4 is of order 12 and is generated from its invariant subgroup $C_2 \times C_2$ which is defined by:

$$A^2 = B^2 = E \quad AB = BA \quad (2.7.6)$$

Simultaneous eigenfunctions of A and B, (Ψ_{jk}) , are readily constructed. The effect of the operator members of the group is defined by the equations

$$A^m B^n \Psi_{jk} = \varepsilon_2^{mj} \varepsilon_2^{nk} \Psi_{jk}$$

The distinct values of jk correspond to

$$\Psi_{00} \quad \Psi_{10} \quad \Psi_{01} \quad \Psi_{11}$$

The group A_4 is generated from this by adding

$$C^3 = E \quad AC = CB \quad BC = CAB \quad (2.7.7)$$

The effect of C on the existing functions can be worked out

$$\begin{aligned} C\Psi_{jk} &= \Phi_{k \ j+k} \\ C\Phi_{k \ j-k} &= \theta_{j+k \ j} \end{aligned} \quad (2.7.8)$$

Then

$$\begin{aligned} C\Psi_{00} &= \Phi_{00} \\ C^2\Psi_{00} &= \theta_{00} \end{aligned}$$

and the three functions may be symmetry readapted to give simultaneous eigenfunctions of A, B and C.

$$\begin{aligned} \Psi_{000} &= \Psi_{00} + \Phi_{00} + \theta_{00} \\ \Psi_{001} &= \Psi_{00} + \omega\Phi_{00} + \omega^*\theta_{00} \\ \Psi_{00-1} &= \Psi_{00} + \omega^*\Phi_{00} + \omega\theta_{00} \end{aligned} \quad (2.7.9)$$

where $\omega = \exp(2\pi i/3)$ and

$$A^m B^n C^p \Psi_{00k} = \varepsilon_3^{pk} \Psi_{00k}$$

Again,

$$C\Psi_{10} = \Phi_{01}$$

$$C^2\Psi_{10} = \theta_{11}$$

and the set of functions $\Psi_{10} \Phi_{01} \theta_{11}$ are degenerate so that they can be eigenfunctions of A and B (as in the form they are written) or eigenfunctions of C (by the transformation in (9) but never be simultaneously eigenfunctions of all three.

The procedure in its most general form yields three sets of degenerate functions

$$\Psi_{10} \quad \Phi_{01} \quad \theta_{11}$$

$$\Phi_{10} \quad \theta_{01} \quad \Psi_{11}$$

$$\theta_{10} \quad \Psi_{01} \quad \Phi_{11}$$

In this way the total set of twelve symmetry adapted functions (equal in number to the order of the group) form a basis for the regular representation of the group (in which each irreducible representation appears a number of times which is equal to its own degeneracy). The procedure has in addition generated the functions so that they are reduced into subsets each corresponding to an irreducible representation.

It is noted that within the degenerate representation, the functions are classified with respect to $C_2 \times C_2$ so that each function is uniquely classified. Finally when triply degenerate sets of functions are written, they are always written in the order 10, 01, 11 for ready identification.

The equations summarised here (the group generators and the symmetry adapted functions) enable the class structure to be deduced and the character table for irreducible representations to be constructed.

The class structure is

E

A B AB

C AC BC ABC

 C^2 AC^2 BC^2 ABC^2

and the character table

A_4	E	3A	4C	$4C^2$
Γ_{000}	1	1	1	1
Γ_{001}	1	1	ω	ω^*
Γ_{00-1}	1	1	ω^*	ω
$\Gamma_{(10,01,11)}$	3	-1	0	0

The group may be recognised as the point group T , the group of rotations of a regular tetrahedron.

The group T_d .

Extension to the full group of the tetrahedron T_d is achieved by adding a fourth element D such that

$$D^2 = E \quad AD = DA \quad BD = DAB \quad CD = DC^2 \quad (2.5.10)$$

The effect of the new element D on the non degenerate functions is

$$D\Psi_{00j} = \Psi_{00-j}$$

For the value $j = 0$ the symmetry behavior with respect to A , B and C is maintained on augmentation to T_d and two non degenerate basis functions result;

$$\Psi_{000k} \quad k = 0, 1.$$

However, for the value $j = \pm 1$ the effect of D is to interchange the two functions and a degeneracy results. The degenerate functions are denoted

$$\Psi_{001}, \Phi_{00-1}$$

The effect of D on the triply degenerate functions can be shown to be

$$D\Psi_{pq} = \alpha_{p+q}$$

So that

$$D\Psi_{10} = \alpha_{11}$$

$$D\theta_{01} = \gamma_{01}$$

$$D\Phi_{11} = \beta_{10}$$

Combinations can be taken so that the functions are simultaneous eigenfunctions of A, B and D but not of C. However, combinations can be taken in such a way so that the symmetry with respect to C is maintained;

$$(\Psi_{10} \pm \beta_{10}) \quad (\theta_{01} \pm \gamma_{01}) \quad (\Phi_{11} \pm \alpha_{11})$$

The result is two sets of triply degenerate functions.

The class structure for the group T_d is

Class								Order
E								1
A	B	AB						2
C	AC	BC	ABC	C^2	AC^2	BC^2	ABC^2	3
D	AD	CD	ABCD	C^2D	BC^2D			2
BD	ABD	ACD	BCD	AC^2D	ABC^2D			4

The character table is

T_d	E	3A	8C	6D	6BD
Γ_{0000}	1	1	1	1	1
Γ_{0001}	1	1	1	-1	-1
$\Gamma_{001,00-1}$	2	2	-1	0	0
$\Gamma_{10,01,11,0}$	3	-1	0	1	-1
$\Gamma_{10,01,11,1}$	3	-1	0	-1	1

2.7.3. A group of order twenty.

A further less familiar group is of order 20. It is built onto

$$D_5: \quad A^5 = B^2 = E \quad AB = BA^4$$

by addition of

$$C^2 = B \quad AC = CA^2 \quad BC = CB$$

In effect the five two-fold cycles of the dihedral group are converted to four-fold cycles.

The irreducible basis functions of D_5 include two non degenerate basis functions

$$\Psi_{0k} = \Psi_0 + \varepsilon_2^k \Phi_0 \quad k = 0, 1$$

and two different pairs of degenerate functions

$$\Psi_1, \Phi_{-1}$$

$$\Psi_2, \Phi_{-2}$$

which are related by

$$B\Psi_j = \Phi_j$$

$$B\Phi_{-j} = \Psi_j \quad j = 1, 2$$

Addition of C gives

$$A(C\Psi_j) = CA^2\Psi_j = \varepsilon_4^{2j}(C\Psi_j)$$

Remembering that $C^2 = B$, the full cycle becomes

$$C\Psi_j = \alpha_{2j}$$

$$C\alpha_{2j} = C^2\Psi_j = B\Psi_j = \Phi_{-j}$$

$$C\Phi_{-j} = C^3\Psi_j = BC\Psi_j = B\alpha_{2j} = \beta_{-2j}$$

$$C\beta_{-2j} = C^4\Psi_j = \Psi_j$$

The result is a four dimensional irreducible representation linking 1, 2, -1, -2.

When $j = 0$, simultaneous eigenfunctions of C can be constructed.

The class structure and orders are

<u>Class</u>	<u>Order</u>
E	1
A A ² A ³ A ⁴	5
B AB A ² B A ³ B A ⁴ B	2
C AC A ² C A ³ C A ⁴ C	4
BC ABC A ² BC A ³ BC A ⁴ BC	4

The character table is

	E	4A	5B	5C	5BC
Γ_{00}	1	1	1	1	1
Γ_{02}	1	1	1	-1	-1
Γ_{01}	1	1	-1	i	$-i$
Γ_{0-1}	1	1	-1	$-i$	i
$\Gamma_{(1,2,-1,-2)}$	4	-1	0	0	0

(The character -1 arises for A in the four fold degenerate representation because in general the sum of all the n^{th} roots of 1 except +1 is always -1).

APPENDICES.

A2.1 Construction of eigenfunctions of a cyclic operator.

Determination of the coefficients c_m in $\sum_m c_m \theta_m$ (Equation 2.3.6).

If $\sum_m c_m \theta_m$ is an eigenfunction of the cyclical operator A then

$$\begin{aligned} A \left[\sum_m c_m \theta_m \right] &= \varepsilon_M^p \left[\sum_m c_m \theta_m \right] \\ &= \exp \left(\frac{2\pi i p}{M} \right) \left[\sum_m c_m \theta_m \right] \end{aligned} \quad (\text{A2.1.1})$$

Note also that

$$\begin{aligned} A \left[\sum_m c_m \theta_m \right] &= \sum_m c_m \theta_{m+1} = \sum_m c_{m-1} \theta_m \\ \therefore \sum_m c_{m-1} \theta_m &= \exp \left(\frac{2\pi i p}{M} \right) \left[\sum_m c_m \theta_m \right] \end{aligned} \quad (\text{A2.1.2})$$

Comparing coefficients of θ_m

$$c_{m-1} = \exp \left(\frac{2\pi i p}{M} \right) c_m \quad (\text{A2.1.3})$$

This suggests that c_m itself has the form

$$c_m = \exp \left(\frac{2\pi i m n}{M} \right)$$

where m refers to the position in the cycle and n is an unknown quantity.

The coefficient c_{m-1} refers to the position (m-1) in the cycle

$$\therefore c_{m-1} = \exp \left(\frac{2\pi i (m-1)n}{M} \right) \quad (\text{A2.1.4})$$

Comparing (3) and (4)

$$\exp\left(\frac{2\pi imn}{M}\right)\exp\left(\frac{-2\pi in}{M}\right) = \exp\left(\frac{2\pi ip}{M}\right)\exp\left(\frac{2\pi imn}{M}\right)$$

$$\therefore -n = p$$

$$\text{Hence } c_m \text{ has the form } \exp\left(\frac{-2\pi ipm}{M}\right)$$

$$\text{i.e. } c_m = \varepsilon_M^{pm*}$$

So we have

$$A\left[\sum_m \exp\left(\frac{-2\pi ipm}{M}\right)\theta_m\right] = \exp\left(\frac{2\pi ip}{M}\right)\left[\sum_m \exp\left(\frac{-2\pi ipm}{M}\right)\theta_m\right]$$

or

$$A\left[\sum_m \varepsilon_M^{pm*}\theta_m\right] = \varepsilon_M^p\left[\sum_m \varepsilon_M^{pm*}\theta_m\right]$$

Eigenfunctions of A have the form

$$\Psi_p = N\sum_m \exp\left(\frac{-2\pi ipm}{M}\right)\theta_m \quad (\text{A2.1.5})$$

or

$$\Psi_p = \left(N\sum_m \varepsilon_M^{pm*} A^m\right)\theta_0 \quad (\text{A2.1.6})$$

where the entity in brackets is called a projection operator.

A2.2 Proof that the eigenfunctions of a cyclic operator are orthogonal.

Proof that $\int \Psi_p^* \Psi_q d\tau = \delta_{pq}$ (equation 2.3.8).

where Ψ_p and Ψ_q are eigenfunctions of A , the cyclic operator.

$$\begin{aligned} \int \Psi_p^* \Psi_q d\tau &= \int \left(\sum_m \exp\left(\frac{2\pi i p m}{M}\right) \theta_m^* \right) \left(\sum_n \exp\left(\frac{-2\pi i q n}{M}\right) \theta_n \right) d\tau \\ &= \sum_{m,n} \exp\left(\frac{2\pi i (p m - q n)}{M}\right) \int \theta_m^* \theta_n d\tau \\ &= \sum_{m=0}^{M-1} \sum_{n=0}^{M-1} \exp\left(\frac{2\pi i (p - q)m}{M}\right) \exp\left(\frac{2\pi i q(m - n)}{M}\right) \int \theta_m^* \theta_n d\tau \end{aligned}$$

Let $\bar{n} = m - n$ (i.e. $n = m - \bar{n}$)

Transform $n \rightarrow \bar{n}$ including summation index

$$\int \Psi_p^* \Psi_q d\tau = \sum_{m=0}^{M-1} \sum_{\bar{n}=0}^{M-1} \exp\left(\frac{2\pi i (p - q)m}{M}\right) \exp\left(\frac{2\pi i q \bar{n}}{M}\right) \int \theta_m^* \theta_{m-\bar{n}} d\tau$$

The integral can only depend on the difference of the two indices since the system has cyclic symmetry and therefore it is independent of the value of m . Then m may be given any convenient value say $m = 0$ and the summations may be factored.

$$\begin{aligned} \int \Psi_p^* \Psi_q d\tau &= \left(\sum_m \exp\left(\frac{2\pi i (p - q)m}{M}\right) \right) \left(\sum_{\bar{n}} \exp\left(\frac{2\pi i q \bar{n}}{M}\right) \int \theta_0^* \theta_{-\bar{n}} d\tau \right) \\ &= M \delta_{pq} \left(\sum_{\bar{n}} \exp\left(\frac{2\pi i q \bar{n}}{M}\right) \int \theta_0^* \theta_{-\bar{n}} d\tau \right) \end{aligned}$$

which proves the functions are orthogonal.

CHAPTER THREE: MANY DIMENSIONAL POINT GROUPS.

3.1 Introduction.

In applications of group theory to chemistry, emphasis is placed on the geometrical structures of molecules and crystals using the corresponding three dimensional point and space groups. More recent developments have led to the use of higher dimensional point and space groups in theories of such phenomena as quasi-crystals [8] and incommensurate solids [9].

The solution of three dimensional problems is facilitated because it is possible to visualise the system under consideration. When higher dimensional geometries are involved the geometrical picture is impossible to visualise and a purely mathematical approach is required.

The theory introduced in the last chapter can be adapted to generate point groups of arbitrarily high dimension directly. In three dimensions the notion of representing a geometrical symmetry operation by an orthogonal matrix is very familiar. An extension to higher dimensions follows quite naturally.

The theory already developed leads to sets of irreducible basis functions for the group under consideration. These are readily converted to unitary matrix irreducible representations of the group. The additional theory discussed in this chapter enables groups of orthogonal matrices to be constructed by appropriate combination and transformation of the irreducible representations. Such a group of orthogonal matrices can always be interpreted as a point group: the dimensionality of the space being equal to the order of the matrices involved.

For a particular abstract group, point groups may be constructed for all dimensionalities down to a minimum value which is characteristic of the group.

Attention will principally be confined to this minimum dimensional point group but an indication will be given of how all possible higher dimensional point groups may be generated.

In three dimensional problems, all possible symmetry operations may be described in terms of rotations and reflections only. It is possible to evolve a classification of symmetry operations in higher dimensions using the same terminology and hence to achieve a partial visualisation of the geometrical properties of the corresponding point groups. This classification is developed in the next section.

3.2 Classification of Operations in Many Dimensional Point Groups.

In elementary accounts of group theory [2], it is usual to express symmetry operations in terms of matrices. In this way the matrix equation

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad (3.2.1)$$

represents the effect on a point (xyz) of a rotation of the space through an angle θ around the z axis. It is moved to a new point (x'y'z'). The 3x3 matrix can be taken to stand for the symmetry operation referred to a set of Cartesian coordinates chosen in this particular way. It is an orthogonal matrix i.e. in general its (real) elements a_{ij} satisfy the equations

$$\sum_k a_{ik} a_{jk} = \delta_{ij} \quad (3.2.2)$$

and the determinant of its elements is ± 1 . Equation (2) implies that the inverse of an orthogonal matrix is equal to its transpose.

An orthogonal matrix is a special example of a unitary matrix, whose determinant is also ± 1 but whose (complex) elements a_{ij} satisfy

$$\sum_k a_{ik} a_{jk}^* = \delta_{ij} \quad (3.2.3)$$

The inverse of a unitary matrix is the transpose of its complex conjugate matrix. In this way an orthogonal matrix is a unitary matrix whose elements are all real.

Equation (1) may be written in the more compact general form:

$$\underline{r}' = A \underline{r} \quad (3.2.4)$$

A vector \underline{r} is transformed by an orthogonal matrix A into a vector \underline{r}' .

The particular entries in the matrix A depend on the choice of coordinate axis directions. A change in the directions gives rise to an equivalent matrix. Thus if

$$\underline{s} = T\underline{r}$$

in which \underline{s} is the vector \underline{r} written with respect to axes transformed by the orthogonal matrix T

$$\underline{s}' = B\underline{s}$$

where

$$B = TAT^{-1}$$

is equivalent to A (i.e. describes the same symmetry operations as A) with respect to the new coordinate axes.

Certain properties of the symmetry operation are invariant under the transformation, in particular the value of the determinant and the character χ i.e. the sum of the diagonal elements. In this way for the example given

$$\chi = \sum_j a_{jj} = \sum_j b_{jj}$$

Again, referring to the three dimensional point groups, it is well known that all symmetry operations can be classified as rotations (C in the Schönflies notation) and rotation-reflections (S). The pure rotations (C) are characterised by determinant $+1$ and the rotation-reflections (S) by determinant -1 . Symmetry operations in the general many dimensional case can be classified according to the value of the determinant ($+1$ or -1) and can be described using the terms rotation and reflection.

The treatment [12, 13] begins by recalling that an orthogonal matrix A always has an equivalent diagonal matrix, the elements of which are the distinct roots of the equation

$$|A - \lambda I| = 0$$

where I is the identity matrix. The vertical bars indicate the determinant of the matrix so that the equation represents a polynomial of order n in the unknown λ .

For the matrix given in (1) the three roots are found to be

$$+1, \quad e^{i\theta}, \quad e^{-i\theta}$$

The occurrence of complex quantities indicates that the diagonal matrix is unitary, i.e. its elements satisfy equation (3).

Correspondingly, the transformation matrix T to the diagonal matrix Λ

$$\Lambda = TAT^{-1}$$

becomes unitary.

The pair of values $e^{i\theta}$ and $e^{-i\theta}$ is diagnostic of a rotation through θ in a plane (in this case the xy plane). The diagonalised form separates complex axes $(x+iy)$ and $(x-iy)$.

These ideas can be generalised. If an orthogonal matrix of any dimensionality is diagonalised, the diagonal elements may only take the following values

$$+1; \quad -1; \quad \text{or the pair } e^{i\theta} \text{ and } e^{-i\theta}$$

The determinant of a diagonal matrix is clearly the product of the diagonal elements.

The value of any combination of the permitted elements is ± 1 as required for a unitary matrix.

Each of the permitted diagonal elements can be given a simple geometrical interpretation which persists however high the dimensionality of the space being considered.

The value $+1$ corresponds to a (real) direction in the space which is left unchanged by the symmetry operation. It will be referred to as an identity (direction).

The value -1 corresponds to a (real) direction which is reversed in sign by the symmetry operation. In three dimensional language it is conventional to speak of a

reflection plane. This is a passive convention emphasising the entity which is left unchanged. It is equally permissible to adopt an active convention and refer to a reflection line: the line in three dimensions being normal to the plane and reversed in sign. This convention can be used to define a reflection in any number of dimensions. A reflection line refers to a single direction which is altered in sign. In a pure reflection, the $(n-1)$ dimensional subspace orthogonal to the line is left unchanged. In this way the value -1 will correspond to a reflection (direction).

It has been seen that the complex conjugate pair $e^{i\theta}$ and $e^{-i\theta}$ is associated with rotation through θ . Again following an active convention, in three dimensions it is emphasised that rotation takes place in a plane (as opposed to round an axis). A generalised rotation in any number of dimensions refers to a plane and in a pure rotation the $(n-2)$ dimensional subspace orthogonal to the plane is left unchanged. A pair of eigenvalues $e^{i\theta} e^{-i\theta}$ is then diagnostic of a rotation plane.

Since these are the only possibilities a generalised notation using (identity) reflection and rotation only can be built up. Operations are divided according to the value of the determinant $+1$ or -1 .

Beginning in 1-dimension, there are only two possibilities

+1	-1
Identity	Reflection

In two dimensions, determinant $+1$ is achieved by the pair $e^{i\theta}, e^{-i\theta}$ (a rotation).

Determinant -1 can only be maintained by adding $+1$

$e^{i\theta}$	$e^{-i\theta}$	+1	-1
Rotation		(Identity)-reflection	

In three dimensions, determinant +1 can only be maintained by adding +1, determinant -1 by replacing +1 by the pair $e^{i\theta}, e^{-i\theta}$

$$+1 \quad e^{i\theta} \quad e^{-i\theta} \quad \dots \quad e^{i\theta} \quad e^{-i\theta} \quad -1$$

(Identity)-rotation

Rotation-reflection

In four dimensions, determinant +1 is maintained by replacing +1 by $e^{i\phi} e^{-i\phi}$ and -1 can only be maintained by adding +1

$$e^{i\theta} \quad e^{-i\theta} \quad e^{i\phi} \quad e^{-i\phi} \quad +1 \quad e^{i\theta} \quad e^{-i\theta} \quad -1$$

Rotation-rotation

(Identity)-rotation-reflection

Higher dimensionalities are reached by repeating the procedure i.e. either

- a) adding identity if it does not occur
- b) replacing identity by rotation if it does occur.

It will be seen that only one essentially new symmetry type is produced for each dimension added. All +1 symmetry operations are compounded from rotations (and the identity) only. All -1 symmetry operations always contain one reflection direction.

The compound rotation-rotation symmetry element type which appears in four dimensions can be pictured in a relatively straight forward way. Just as in two dimensions, two orthogonal lines meet only in one point, so in four dimensions, two orthogonal planes intersect only in one point. The implication is that independent rotations (indicated by independent values of the angles ϕ and θ) can take place in the two planes. All +1 symmetry operations in four dimensions can be expressed in this way.

The classification just given is compact in the sense that, for any dimension, symmetry operations can be allocated to one of only two types. Particular examples occur which have special significance. Thus in three dimensions, a rotation-reflection through 0

reduces to the three diagonal elements $+1 +1 -1$. This is identifiable as a reflection line and is given the special symbol σ in the Schönflies notation. On the other hand, a rotation-reflection through π reduces to $-1 -1 -1$. This is the familiar inversion (denoted by i). The point is that there is now an ambiguity in the interpretation of the rotation-reflection. Is the rotation in the xy plane and the reflection along z or is the rotation in the xz plane and the reflection along y ? Clearly there is no physical distinction between these two possibilities. Similar, but much less familiar, special cases arise in higher dimensions. Thus, in four dimensions, for a rotation-rotation the rotation angle in one of the planes may be 0 leading to the diagonal elements $+1 +1 e^{i\theta} e^{-i\theta}$. This special case shows that the lower dimensional possibility of a simple rotation is implicitly contained in the four dimensional classification. This is always the case: all lower dimensional operations are contained in higher order type.

A second special case corresponds to rotations of π in both planes leading to the diagonal values $-1 -1 -1 -1$. This is the four dimensional analogue of the inversion and contains a similar ambiguity. Is the operation a π rotation in xy together with a π rotation in zw or a π rotation in the xz plane together with a π rotation in the yw plane? Once again there is no physical distinction. It might be anticipated that point groups which are peculiarly four dimensional may reflect this ambiguity.

A more subtle ambiguity arises when the two angles in a double rotation are equal so that the elements of the equivalent diagonal matrix become $e^{i\theta} e^{-i\theta} e^{i\theta} e^{-i\theta}$ and the repeated roots indicate that the choice of underlying equivalent eigenvector is not uniquely determined.

If attention is restricted to orthogonal matrices, only a partial diagonalisation is possible giving the following form

$$\begin{pmatrix} c & -s & 0 & 0 \\ s & c & 0 & 0 \\ 0 & 0 & c & -s \\ 0 & 0 & s & c \end{pmatrix}$$

in which $c = \cos\theta$ and $s = \sin\theta$.

If attention is focussed on the upper diagonal block the resulting 2×2 matrix describes a rotation through θ in the xy plane. It is noted that the matrix is independent of the precise pair of orthogonal directions chosen for x and y i.e. the rotation matrix is invariant under a rotation of the Cartesian axis directions. Moreover in the four dimensional case, this invariance remains whether the rotation angle in the zw plane is the same or not. The axes in the zw plane may of couse also be rotated independently without changing the matrix.

It follows that any additional invariances which result from the equi-angular double rotation can be expressed as a coordinate rotation in the plane xz plus a coordinate rotation in yw . It can be shown that invariance is only maintained if the rotation angles are the same. In terms of a matrix equation

$$\begin{pmatrix} p & 0 & q & 0 \\ 0 & p & 0 & q \\ -q & 0 & p & 0 \\ 0 & -q & 0 & p \end{pmatrix} \begin{pmatrix} c & -s & 0 & 0 \\ s & c & 0 & 0 \\ 0 & 0 & c & -s \\ 0 & 0 & s & c \end{pmatrix} \begin{pmatrix} p & 0 & -q & 0 \\ 0 & p & 0 & -q \\ q & 0 & p & 0 \\ 0 & q & 0 & p \end{pmatrix} = \begin{pmatrix} c & -s & 0 & 0 \\ s & c & 0 & 0 \\ 0 & 0 & c & -s \\ 0 & 0 & s & c \end{pmatrix}$$

Where $p^2 + q^2 = 1$.

The above discussion is not quite complete in that only transformations which leave the whole standard matrix invariant are discussed. Once again reverting to the 2×2 case, the transformation

$$\begin{pmatrix} m & n \\ n & -m \end{pmatrix} \begin{pmatrix} c & -s \\ s & c \end{pmatrix} \begin{pmatrix} m & n \\ n & -m \end{pmatrix} = \begin{pmatrix} c & s \\ -s & c \end{pmatrix}$$

(with $m^2 + n^2 = 1$) represents a rotation-reflection of the axes and leads to an exchange between the terms s and $-s$. The transformation matrix has value -1 and the 'handedness' of the pair of axes is changed: one of them being reversed in sign. There are several additional possibilities in the four dimensional case of transformations which preserve the partially diagonalised form but not necessarily the relative positions of s and $-s$. These are not listed explicitly here.

3.3 A simple Example of a Four Dimensional Point Group.

To illustrate the classification introduced in the last section, a characteristic four dimensional point group will be built up in an intuitive way, making a contrast with the analytical methods used in other parts of the thesis.

It has been remarked that the four dimensional inversion (eigenvalues -1 -1 -1 -1) is formally equivalent to two rotations through π in orthogonal planes, but that the location of the planes is totally indeterminate. The notion is that the “square root” of the inversion is then also not uniquely defined but may be a double ninety degree rotation either in the xy and zw planes or in the xz and yw planes or in the xw and yz planes. We start a set including all three of these symmetry operations and construct a group from them. For the present purpose a non-standard notation is used.

$$C(xy,zw) \quad C(xz,yw) \quad C(xw,yz)$$

The square of each operator is the four dimensional inversion i and the cube of each gives the corresponding double rotation through minus ninety degrees.

$$C^{-1}(xy,zw) \quad C^{-1}(xz,yw) \quad C^{-1}(xw,yz)$$

The fourth power of each operator gives the identity E .

The group is completed by considering products of different C operators. If the operators are represented by the following matrices

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

E

$$\begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}$$

C(xz,wy)

$$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

C(xy,zw)

$$\begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

C(xw,yz)

$$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

i

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$$

C⁻¹(xy,zw)

$$\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

C⁻¹(xz,wy)

$$\begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$$

C⁻¹(xw,yz)

it is found that

$$C(xy,zw)C(xz,wy) = C(xw,yz)$$

$$C(xz,wy)C(xy,zw) = C^{-1}(xw,yz)$$

It can then be shown that all possible products of members of the set are implied by the

relations already given and that the eight operations form a group. The group so

constructed is isomorphous with the quaternion group discussed in section 2.7.1 i.e.

there is a one-to-one correspondence between the matrices given here and the elements

of the quaternion group. If C(xz,wy) is replaced by the symbol A and C(xy,zw) is

replaced by B then the matrices can be seen to satisfy the relations $A^4 = E$, $B^2 = A^2$,

$$AB = BA^3.$$

3.4 From Irreducible Basis Functions To Orthogonal Matrix groups.

In this section, the formal connection will be made between the solvable group method as described in chapter two and the construction of point groups (orthogonal matrix groups).

The method of chapter two essentially shows how basis functions can be constructed which are simplified as far as possible with respect to the group under consideration.

The parallel between this approach and the more familiar language of irreducible representations and character tables has been discussed. To make the connection more clear, let $\phi_k^{(r)}$ be the k^{th} member of an n -fold degenerate set of basis functions underlying an irreducible representation (r) constructed by the solvable group method.

Then the effect of F a member of the group can be written

$$F\phi_k^{(r)} = \sum_{j=1}^n c_{jk}^{(r)}(F)\phi_j^{(r)} \quad (3.4.1)$$

i.e. a linear combination of the basis functions with coefficients c results. It is a characteristic of the present method that for a given value of k , all the coefficients are zero except one, which is a root of unity (and therefore usually complex). For the present purpose it is sufficient to note that the matrix $C(F)$ is unitary.

Suppose that the group elements are related by

$$T = SF$$

It was shown in section 2.2 that

$$c_{jl}(T) = \sum_k c_{jk}(S)c_{kl}(F) \quad (3.4.2)$$

so that the set of matrices C forms a matrix representation of the group. Since the set of basis functions is irreducible, the matrix representation is irreducible. The

corresponding characters are readily deduced and a character table may be constructed. It is recalled that the method of solvable groups yields all possible irreducible representations.

The problem is how to construct from the matrix representations, groups of orthogonal matrices. An individual matrix representation, consisting of unitary matrices, would need to fulfil two conditions to be able to yield an orthogonal matrix group.

- a) It must be possible to find a transformation matrix which simultaneously converts all the unitary matrices to a corresponding real form i.e. to orthogonal matrices.
- b) The representation should be faithful i.e. all the matrices should be different.

In these circumstances, the set of matrices form a group under matrix multiplication which is isomorphous with the abstract group under consideration.

With respect to the first of these, it is always possible to construct a representation which does have an equivalent real form by taking the direct sum of an irreducible representation plus its complex conjugate. It proves possible to classify representations of three different kinds [28, 36].

First kind. The representation is equivalent to a real form and is equivalent to its complex conjugate.

Second kind. The representation is not equivalent to a real form but is equivalent to its complex conjugate representation.

Third kind. The representation is not equivalent to a real form and is not equivalent to its complex conjugate.

The kind to which a particular *irreducible* representation belongs can be determined by a simple algebraic test using the characters.

$$\begin{aligned} &= g \quad \text{for first kind representations.} \\ \sum_A \chi(A^2) &= -g \quad \text{for second kind representations.} \\ &= 0 \quad \text{for third kind representations.} \end{aligned} \tag{3.4.3}$$

Here g is the order of the group.

For the present purpose, a first kind representation is equivalent to a real matrix form as it stands. Second and third kind representations must be combined with their complex conjugates.

It is not always necessary to perform the test (3) explicitly. First and second kind representations only have real characters. Third kind representations always have some complex characters. Furthermore, second kind representations are always of even order and are restricted to combinations of a few group types, which include quaternion and bicyclic groups considered in this work.

The second condition, that the desired “point group” representation should be faithful, can also be investigated using the character table. A representation is not faithful if the character of any group member other than the identity is equal to the character of the identity, since this would imply that the identity matrix occurs more than once in the representation.

An orthogonal matrix group can then be constructed by taking an appropriate combination of irreducible representations:

- 1) so that there are no repeated identity characters
- 2) so that any second or third kind representation is balanced by addition of its complex conjugate.

The matrix group so constructed will usually be in an equivalent unitary form. The method of transforming to real form will become clear through examples.

3.5 Examples of Point Groups and a Classification of minimum Point Groups.

The theory connecting solvable group basis functions and point groups will now be illustrated by a number of examples. Attention will mainly be confined to the “minimum” point group i.e. to the group of lowest possible dimensionality consistent with the properties of the underlying abstract group. A classification of such minimum point groups will be developed. An indication will also be given of how all possible higher dimensional point groups may be constructed.

The group C_2 generated by

$$A^2 = E$$

has one non-totally symmetric irreducible representation with characters

$$\chi(E) = +1 \quad \chi(A) = -1$$

This representation is clearly faithful and orthogonal and hence represents a one dimensional point group.

For the group C_3 ($A^3 = E$), the characters are

	E	A	A ²
Γ_0	1	1	1
Γ_1	1	ω	ω^*
Γ_{-1}	1	ω^*	ω

$$\omega = \varepsilon_3^1 = -1/2 + i\sqrt{3}/2$$

Both Γ_1 and Γ_{-1} are clearly faithful but unitary. Explicit use of the test (3.4.3) shows that they are third kind representations. The direct sum of Γ_1 and Γ_{-1} gives matrices

$$\begin{matrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} \omega & 0 \\ 0 & \omega^* \end{pmatrix} & \begin{pmatrix} \omega^* & 0 \\ 0 & \omega \end{pmatrix} \\ E & A & A^2 \end{matrix}$$

which must be equivalent to a set of orthogonal matrices. The transformation

$$TAT^{-1}$$

$$\text{where } T = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -i & i \end{pmatrix} \text{ and } T^{-1} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ 1 & -i \end{pmatrix}$$

leads to

$$\begin{matrix} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} & \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \\ E & A & A^2 \end{matrix}$$

A two dimensional point group results. It is readily seen that all higher cyclic groups C_n will behave in essentially the same way as C_3 i.e. they lead to a two dimensional point group. It is also clear that there is a distinction between cycles of order two, with real roots of unity, and of all other orders which have complex roots of unity.

$$\text{For } C_2 \times C_2: (A^2 = B^2 = E \quad AB = BA)$$

the character table is

$C_2 \times C_2$	E	A	B	AB
Γ_{00}	1	1	1	1
Γ_{01}	1	1	-1	-1
Γ_{10}	1	-1	1	-1
Γ_{11}	1	-1	-1	1

No representation is faithful; all are of the first kind (orthogonal). A faithful representation can be constructed by adding any two non-totally symmetric representations, for example

$$\Gamma_{01} + \Gamma_{10}$$

and a two dimensional point group results. The orthogonal matrices are

$$\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}_E \quad \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_A \quad \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}_B \quad \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}_{AB}$$

For the dihedral group D_3 ($A^3 = B^2 = E$ $AB = BA^2$). The degenerate irreducible representation with characters

$$\begin{array}{ccc} E & 2A & 3B \\ 2 & -1 & 0 \end{array}$$

is faithful and of the first kind. There is therefore a corresponding two dimensional point group. The set of unitary matrices yielded by the solvable group treatment may be generated from

$$\begin{pmatrix} \omega & 0 \\ 0 & \omega^* \end{pmatrix}_A \quad \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_B$$

and the same transformation as was used for C_3 gives the orthogonal generating matrices

$$\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}_A \quad \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_B$$

all higher dihedral groups D_n behave similarly.

Three two dimensional point groups have been derived but each has its own distinctive features which may be used as the basis of a classification. Thus, C_3 point group is constructed from a one dimensional third kind representation plus its complex conjugate; $C_2 \times C_2$ by addition of two different one dimensional first kind representations and D_3 from a single first kind two dimensional representation. A notation may be devised

Group	Minimum point group type
C_3	$(1d + 1d^*)$
$C_2 \times C_2$	$1d + 1d$
D_3	$2d$

The brackets indicate that representations within are related. Absence of brackets indicates the representations are different.

Proceeding to a few further examples, the character table for $C_4 \times C_2$

($A^4 = B^2 = E$ $AB = BA$) has the form

$C_4 \times C_2$	E	A	A^2	A^3	B	AB	A^2B	A^3B
Γ_{00}	1	1	1	1	1	1	1	1
Γ_{01}	1	1	1	1	-1	-1	-1	-1
Γ_{20}	1	-1	1	-1	1	-1	1	-1
Γ_{21}	1	-1	1	-1	-1	1	-1	1
Γ_{10}	1	i	-1	$-i$	1	i	-1	$-i$
Γ_{11}	1	i	-1	$-i$	-1	$-i$	1	i
Γ_{-10}	1	$-i$	-1	i	1	$-i$	-1	i
Γ_{-11}	1	$-i$	-1	i	-1	i	1	$-i$

Combining previous results, addition of Γ_{10} and Γ_{-10} fixes up the C_4 part of the group

but the representation is still not faithful. Addition of Γ_{01} removes this last difficulty.

$\Gamma_{01} + \Gamma_{10} + \Gamma_{-10}$ then gives a three dimensional point group which may be recognised as

C_{4h} in the Schönflies notation.

The quaternion group Q

$$(A^4 = E \quad B^2 = A^2 \quad AB = BA^3)$$

has a two dimensional irreducible representation

E	A^2	$2A$	$2B$	$2AB$
2	-2	0	0	0

the corresponding matrices were given in section (2.7.1). The representation is clearly

faithful, but on application of test (3.4.3) proves to be second kind. An orthogonal

matrix representation can then be found by adding a second two dimensional

component of the same kind. The unitary matrix group is then

$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \\ 0 & 0 & -i & 0 \\ 0 & 0 & 0 & i \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$	$\begin{pmatrix} -i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \\ 0 & 0 & i & 0 \\ 0 & 0 & 0 & -i \end{pmatrix}$
E	A	A^2	A^3

$\begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & -i & 0 & 0 \\ -i & 0 & 0 & 0 \\ 0 & 0 & 0 & i \\ 0 & 0 & i & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & i & 0 & 0 \\ i & 0 & 0 & 0 \\ 0 & 0 & 0 & -i \\ 0 & 0 & -i & 0 \end{pmatrix}$
B	AB	A^2B	A^3B

The transformation TAT^{-1} where

$$T = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ -i & 0 & i & 0 \\ 0 & -i & 0 & i \end{pmatrix} \quad T^{-1} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & i & 0 \\ 0 & 1 & 0 & i \\ 1 & 0 & -i & 0 \\ 0 & 1 & 0 & -i \end{pmatrix}$$

generates an orthogonal matrix group with matrices

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

E A A² A³

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

B AB A²B A³B

The quaternion minimum point group is four dimensional and the matrices are seen to be the same as those of the intuitive example set up in section 3.3.

Again the group A₄

$$(A^2 = B^2 = C^3 = E \quad AB = BA \quad AC = CB \quad BC = CAB)$$

has a three dimensional representation

$$\begin{matrix} E & 3A & 4C & 4C^2 \\ 3 & -1 & 0 & 0 \end{matrix}$$

which is both faithful and real. In this case the solvable group treatment leads directly to an orthogonal matrix group and hence a three dimensional point group the generating matrices being

$$\begin{array}{ccc}
 \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} \\
 A & B & C
 \end{array}$$

Notation for the minimum point group type may be extended in an obvious way to cover these examples.

Group	Minimum point group type
$C_4 \times C_2$	$(1d + 1d^*) + 1d$
Q	$(2d + 2d)$
A_4	$3d$

It is noted that only one four dimensional point group has emerged and none of higher order. The point group types for a given value of the dimension cover various combinations of irreducible representations. The examples D_3 and A_4 are particularly simple since there is only a single faithful orthogonal irreducible representation involved. It is recalled that the sum of the squares of the orders of all the irreducible representations is equal to the order of the group and that the dimension of any irreducible representation must be a factor of the order of the group. Therefore the dimension of any irreducible representation must be less than the square root of the order of the group. In this way the smallest possible order for a group with minimum point group type nd is $n(n+1)$. Thus D_3 (type $2d$) is of order 6.

This suggests that a group of order 20, type $4d$, might be found.

The group

$$A^5 = B^2 = E \quad AB = BA^4$$

$$C^2 = B \quad AC = CA^2$$

discussed in section (2.7.3) has a four dimensional faithful representation:

$$\begin{array}{ccccc} E & 4A & 5C^2 & 5C & 5C^3 \\ 4 & -1 & 0 & 0 & 0 \end{array}$$

which on application of test (3.4.3) shows to be of the first kind. The unitary matrix generators yielded by the basic procedure are

$$\begin{array}{ccc} \begin{pmatrix} \varepsilon_5^1 & 0 & 0 & 0 \\ 0 & \varepsilon_5^{1*} & 0 & 0 \\ 0 & 0 & \varepsilon_5^2 & 0 \\ 0 & 0 & 0 & \varepsilon_5^{2*} \end{pmatrix} & \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \\ A & B & C \end{array}$$

which are equivalent to the orthogonal matrices

$$\begin{array}{ccc} \begin{pmatrix} c_j & -s_j & 0 & 0 \\ s_j & c_j & 0 & 0 \\ 0 & 0 & c_{2j} & -s_{2j} \\ 0 & 0 & s_{2j} & c_{2j} \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \\ A & B & C \end{array}$$

in which $c_j = \cos(2\pi j/5)$ $s_j = \sin(2\pi j/5)$

The four dimensional point group derived in this way is relatively easily pictured. The symmetry operator A and its powers corresponds to a double five fold rotation system in the xy and zw planes: the angle of rotation in the zw plane always being twice that in the xy plane. The operation C can be identified as a rotation reflection S_4 : the $\pi/2$ rotation is in the yw plane and the reflection line bisects the x and -z axes. There are five such S_4 systems equivalently disposed around the double five-fold plane system. The whole group can be described as a four dimensional analogue of the dihedral groups found in two and three dimensions.

3.6 The construction of higher than minimum dimensional point groups.

Once the minimum dimensional point group corresponding to a particular abstract group has been established, it is relatively straight forward to construct all possible higher dimensional point groups. A few examples suffice to illustrate the principles involved.

Beginning with C_2 ($A^2 = E$), this group has two irreducible representations with characters:

C_2	E	A
Γ_0	1	1
Γ_1	1	-1

Γ_1 is faithful and real and gives the minimum (one dimensional) point group as already mentioned. In higher dimensions, any combination of irreducible representations gives a point group provided there is at least one Γ_1 component.

Two dimensions: $\Gamma_0 + \Gamma_1 = \text{reflection line}$

$$2\Gamma_1 = 180^\circ \text{ rotation.}$$

Three dimensions $2\Gamma_0 + \Gamma_1 = C_{1h}$

$$\Gamma_0 + 2\Gamma_1 = C_2$$

$$3\Gamma_1 = S_2$$

In three dimensions, the familiar Schönflies symbols serve to identify the groups.

The dihedral group D_4 ($A^4 = B^2 = E$, $AB = BA^3$) has characters

D_4	E	2A	A^2	2B	2AB
Γ_{00}	1	1	1	1	1
Γ_{01}	1	1	1	-1	-1
Γ_{20}	1	-1	1	1	-1
Γ_{21}	1	-1	1	-1	1
$\Gamma_{1,-1}$	2	0	-2	0	0

As for the D_3 group only the doubly degenerate representation is faithful and of the first kind and hence is equivalent to a two dimensional point group.

Three different three dimensional point groups may be constructed by combining

$$\Gamma_{00} + \Gamma_{1,-1} \equiv C_{4v}$$

$$\Gamma_{01} + \Gamma_{1,-1} \equiv D_4$$

$$\Gamma_{20} + \Gamma_{1,-1} \equiv D_{2d}$$

3.7 The four dimensional point groups.

In this section, the possibility of devising a full list of four dimensional point groups using the methods developed here is discussed. Complete lists of point groups are known for one, two and three dimensions and many four dimensional point groups can be constructed from them by extension as shown in the previous section.

First the point groups in lower dimensions are reviewed.

For one dimension there is only one non-trivial group

Minimum group type	Abstract group
1d	C_2

In two dimensions, additional groups are

1d + 1d	$C_2 \times C_2$
(1d + 1d [*])	C_n
2d	D_n

For three dimensions, the point groups are (using the Schönflies notation)

Minimum group type	Abstract group	Point groups
1d	C_2	C_2
		C_{1h}
		S_2
1d + 1d	$C_2 \times C_2$	D_2
		C_{2v}

		C_{2h}
$(1d + 1d^*)$	C_n	C_n
		$S_n(n \text{ even})$
		$C_{nh}(n \text{ odd})$
$2d$	D_n	D_n
		C_{nv}
		$D_{nd}(n \text{ even})$
$1d + 1d + 1d$	$C_2 \times C_2 \times C_2$	D_{2h}
$(1d + 1d^*) + 1d$	$C_n \times C_2$	$C_{nh}(n \text{ even})$
$2d + 1d$	$D_n \times C_2$	D_{nh}
		$D_{nd}(n \text{ odd})$ * Example
$3d$	A_4	T
$3d$	$A_4 \times C_2$	T_h
$3d$	S_4	O
		T_d
$3d$	$S_4 \times C_2$	O_h
$3d$	A_5	I
$3d$	$A_5 \times C_2$	I_h

An interesting observation is that the “intrinsically” three dimensional point groups (i.e. type 3d) are all associated with (or closely related to) the platonic solids. It is also noted that all the groups are solvable except A_5 and $A_5 \times C_2$: the icosahedral groups. It should be possible to list the types of four dimensional point groups in a corresponding way and perhaps find examples of each. All the three dimensional types

may be extended and attention is confined to those types which have minimum four dimensional point group. These are listed below together with examples.

Minimum group type	Abstract group
$1d + 1d + 1d + 1d$	$C_2 \times C_2 \times C_2 \times C_2$
$(1d + 1d^*) + 1d + 1d$	$C_n \times C_2 \times C_2$
$(1d + 1d^*) + (1d + 1d^*)$	$C_n \times C_{n'}$
$2d + 1d + 1d$	$D_n \times C_2 \times C_2$
$2d + (1d + 1d^*)$	$D_n \times C_{n'}$
$2d + 2d$	$D_n \times D_{n'}$
$(2d + 2d)$	Q_n
$(2d + 2d^*)$	
$3d + 1d$	$A_4 \times C_2 \times C_2$
	$S_4 \times C_2 \times C_2$
	$A_5 \times C_2 \times C_2$

The four dimensional point groups are more complicated than those in lower dimensions in a number of important respects. Firstly, the quaternion group Q illustrates that four dimensional groups can be constructed by addition of two equivalent second kind irreducible representations, denoted by $(2d + 2d)$ in the notation introduced earlier. In the same way four dimensional point groups of type $(2d + 2d^*)$ should also be possible.

Secondly, the point group of order 20, introduced in section 2.7.3 and described geometrically in section 3.5 belongs to the 4d type. In three dimensions, all the 3d type

point groups are related to the five regular polyhedra (or Platonic solids). The group of order 20 does not correspond to a four dimensional regular polytope [37] since a unique double plane exists corresponding to the five fold symmetry. The 4d type point group thus covers a wider range of possibilities than in three dimensions.

The four dimensional groups quoted in the last table according to type were constructed by the simple device of forming direct products of lower dimensional groups. It is trivial to write down the character tables of such groups and to deduce from the tables the types and dimensions of possible point groups, in particular the minimum dimensional point groups.

A number of examples are now considered in some detail which are not able to be derived in this simple way. Most are of order sixteen and all are minimum four dimensional point groups. These may be generated starting from a group of order eight, a group which is necessarily invariant. The first few examples start with $C_4 \times C_2$.

$$A^4 = B^2 = E \quad AB = BA$$

First the relations

$$C^2 = E \quad AC = CAB \quad BC = CB$$

are added.

The details of the basis function analysis and full character table are given in appendix 3.1.

There are interlocked 4-fold cycles

$$E \quad A \quad A^2 \quad A^3$$

$$E \quad AB \quad A^2 \quad A^3B$$

and

$$E \quad AC \quad A^2B \quad A^3BC$$

E ABC A^2B A^3C

with the remaining elements

B C A^2C BC A^2BC

in separate 2-fold cycles.

In terms of classes

E A^2 A^2B and B

are in separate classes and the remainder in pairs:

(A, AB) (A^3 , A^3B) (AC, ABC) (A^3BC , A^3C) (C, BC) (A^2C , A^2BC).

It is seen that the fourth order members within a class belong to different cycles.

There are two first kind unfaithful doubly degenerate representations with characters:

	E	2A	A^2	$2A^3$	B	A^2B	2C	2AC	$2A^2C$	$2A^3C$
$\Gamma_{(01,21)}$	2	0	2	0	-2	-2	0	0	0	0
$\Gamma_{(11,-11)}$	2	0	-2	0	-2	2	0	0	0	0

A four dimensional point group of type $2d + 2d$ may be formed. The resulting orthogonal matrices are listed in the following table;

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

E A A² A³

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

B AB A²B A³B

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

C AC A²C A³C

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

BC ABC A²BC A³BC

Closer examination shows that all the matrices have no cross terms between the xy plane and the zw plane. Furthermore, examination of the component 2 x 2 matrices shows that they correspond to the two dimensional point group D₄ of order 8 with each matrix repeated twice. The four dimensional character then comes from the interplay of the two sub-plane systems.

Suppose the 2 x 2 matrices are written symbolically:

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

E P P² P³

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

Q PQ P²Q P³Q

then the matrices of the group of order sixteen can be written in block form, for

example

$$A: \begin{pmatrix} P^3Q & 0 \\ 0 & P \end{pmatrix} = (P^3Q, P)$$

$\begin{pmatrix} E, E \\ E \end{pmatrix}$	$\begin{pmatrix} P^3Q, P \\ A \end{pmatrix}$	$\begin{pmatrix} E, P^2 \\ A^2 \end{pmatrix}$	$\begin{pmatrix} P^3Q, P^3 \\ A^3 \end{pmatrix}$
$\begin{pmatrix} P^2, P^2 \\ B \end{pmatrix}$	$\begin{pmatrix} PQ, P^3 \\ AB \end{pmatrix}$	$\begin{pmatrix} P^2, E \\ A^2B \end{pmatrix}$	$\begin{pmatrix} PQ, P \\ A^3B \end{pmatrix}$
$\begin{pmatrix} Q, P^3Q \\ C \end{pmatrix}$	$\begin{pmatrix} P^3, Q \\ AC \end{pmatrix}$	$\begin{pmatrix} Q, PQ \\ A^2C \end{pmatrix}$	$\begin{pmatrix} P^3, P^2Q \\ A^3C \end{pmatrix}$
$\begin{pmatrix} P^2Q, PQ \\ BC \end{pmatrix}$	$\begin{pmatrix} P, P^2Q \\ ABC \end{pmatrix}$	$\begin{pmatrix} P^2Q, P^3Q \\ A^2BC \end{pmatrix}$	$\begin{pmatrix} P, Q \\ A^3BC \end{pmatrix}$

The geometrical significance of the total 4 x 4 matrix is readily deduced, since it can be broken down into two dimensional subparts. Thus, the matrix

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

in the xy plane corresponds to a reflection line along the bisector of axes x and -y. (It is recalled that the active convention is used: the reflection line changes direction as a result of the reflection.) This will be denoted by $R(\overline{xy})$ in what follows. The negative of the above matrix leads to $R(xy)$ i.e. reflection of the bisector of axes x and y. In this way the following results are found.

E	A	A^2	A^3
$E(xy)$	$R(y)$	$E(xy)$	$R(y)$
$E(yz)$	$C_4(zw)$	$C_2(zw)$	$C_4^3(zw)$

B	AB	A ² B	A ³ B
C ₂ (xy)	R(x)	C ₂ (xy)	R(x)
C ₂ (zw)	C ₄ ³ (zw)	E(zw)	C ₄ (zw)
C	AC	A ² C	A ³ C
R(x \bar{y})	C ₄ ³ (xy)	R(x \bar{y})	C ₄ ³ (xy)
R(w)	R(z \bar{w})	R(z)	R(zw)
BC	ABC	A ² BC	A ³ BC
R(xy)	C ₄ (xy)	R(xy)	C ₄ (xy)
R(z)	R(zw)	R(w)	R(z \bar{w})

It can further be noted that the combination of R and C₄ implies that there is one identity direction and that the operation is equivalent to S₄ in the remaining three dimensional subspace. It is interesting to note that although the orthogonal matrices representing the four dimensional point group show that the xy plane and the zw plane are algebraically uncoupled, geometrically the planes are not independent.

Also the combination of two R elements implies that two orthogonal directions (and therefore a plane) are left unchanged. The remaining two axes define a plane in which each coordinate axis is reversed in sign and thus corresponds to a π rotation in that plane.

All these ideas may be combined to give a composite description which conveys the four dimensional symmetry in three dimensional terms:

a) Four four-fold rotation-reflection systems;

- (i) Rotation (zw) + reflection (x)
- (ii) Rotation (zw) + reflection (y)
- (iii) Rotation (xy) + reflection (zw)
- (iv) Rotation (xy) + reflection (\overline{zw})

b) Four two-fold rotation planes;

- (i) Rotation (xy, z)
- (ii) Rotation($x\overline{y}$, z)
- (iii) Rotation (xy, w)
- (iv) Rotation ($x\overline{y}$, w)

c) The four dimensional inversion (B), which is independent of any other cycle.

As a second example, the following relations are added to $C_4 \times C_2$:

$$C^2 = E \quad AC = CA \quad BC = CA^2B$$

As before, the basic function analysis and character table are in appendix 3.2.

There are four four-fold cycles all with a common second order element:

$$A \quad A^2 \quad A^3$$

$$AB \quad A^2 \quad A^3B$$

$$AC \quad A^2 \quad A^3C$$

$$BC \quad A^2 \quad A^2BC$$

and the remaining elements are second order:

$$B \quad A^2B \quad C \quad A^2C \quad ABC \quad A^3BC$$

In terms of classes

$$E \quad A^2 \quad A \quad A^3$$

are in separate classes and the remainder in pairs:

$$(AB, A^3B) \quad (AC, A^3C) \quad (BC, A^2BC)$$

$$(B, A^2B) \quad (C, A^2C) \quad (ABC, A^3BC)$$

It is noted at once that one of the four cycles is distinct from the other three in that all its elements remain in separate classes.

There are two third kind, faithful, doubly degenerate representations, which are complex conjugates.

	E	A	A ²	A ³	2B	2AB	2C	2AC	2BC	2ABC
$\Gamma_{(10,11)}$	2	2i	-2	-2i	0	0	0	0	0	0
$\Gamma_{(-10,-11)}$	2	-2i	-2	2i	0	0	0	0	0	0

The sum of the two leads to a point group of the type $(2d + 2d^*)$. The equivalent orthogonal matrices are

$$\begin{array}{cccc}
\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix} \\
E & A & A^2 & A^3 \\
C_4(xy)C_4(zw) & & & C_4^3(xy)C_4^3(zw) \\
\\
\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix} & \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \\
B & AB & A^2B & A^3B \\
C_2(zw) & C_4(xy)C_4^3(zw) & C_2(xy) & C_4^3(xy)C_4(zw) \\
\\
\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix} \\
C & AC & A^2C & A^3C \\
R(x\bar{z})R(y\bar{w}) & C_4(xw)C_4^3(yz) & R(xz)R(yw) & C_4^3(xw)C_4(yz) \\
\\
\begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \\
BC & ABC & A^2BC & A^3BC \\
C_4^3(xz)C_4^3(yw) & R(xw)R(y\bar{z}) & C_4(xz)C_4(yw) & R(x\bar{w})R(yz)
\end{array}$$

The matrices all have determinant +1 and so the group consists only of “pure”

rotation-rotations. Following the discussion of the previous group, it is recalled that

two reflection lines are equivalent to a two fold rotation plane.

A composite description of the symmetry elements of the group is given.

a) A unique four-fold cycle generated from the double $\pi/2$ rotation

$$\pi/2(xy) + \pi/2(zw)$$

b) Three related four-fold cycles generated from the double $\pi/2$ rotations:

$$\pi/2(xy) + (-\pi/2)(zw)$$

$$\pi/2 (xw) + (-\pi/2) (yz)$$

$$(-\pi/2) (xz) + (-\pi/2) (yw)$$

All the four-fold cycles are routed through the “four dimensional inversion”.

c) Two two-fold rotation planes in the planes of the unique double four fold rotation:

(i) Rotation (x,y)

(ii) Rotation (z,w)

d) Four two fold rotation planes, containing bisectors of two coordinate axes: x and y always separated; z and w always separated.

(i) Rotation (xz, yw)

(ii) Rotation ($x\bar{z}$, $y\bar{w}$)

(iii) Rotation (xw, $y\bar{z}$)

(iv) Rotation ($x\bar{w}$, yz).

A feature of interest is that the underlying $C_4 \times C_2$ contains two equivalent four fold cycles based on A and AB. These are double $\pi/2$ rotations in the same two planes: but differ since A is associated with $+\pi/2$ in plane zw and AB with $-\pi/2$ in zw. These can be thought of as an enantiometric pair since they differ only in the orientation of one axis.

The augmenting element C affects the two enantiometric operations differently: it commutes with A but not with AB. This can be understood by transforming all three matrices to an axis system which simplifies C:

$$\frac{1}{2} \begin{pmatrix} 1 & 0 & 1 & 0 \\ 1 & 0 & -1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 \end{pmatrix}$$

T C T^{-1}

the transformed matrices are as follows

$$\begin{array}{ccc}
 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \\
 \text{C} & \text{A} & \text{AB} \\
 \text{E(xz)C}_2(\text{yw}) & \text{C}_4(\text{xz})\text{C}_4(\text{yw}) & \text{C}_4(\text{xw})\text{C}_4(\text{yz})
 \end{array}$$

As previously discussed, an equal angle double rotation does not have a unique decomposition into component rotational planes. It is interesting that although both A and AB maintain their reduced form with respect to the new coordinate axes, their enantiometric relationship is no longer apparent. Of more direct interest in the present context is that the rotation planes of C match those of A but not those of AB. Hence A and C commute and AC is described as $(\pi/2)$ in xz plus $(-\pi/2)$ in yw. Correspondingly C and AB do not commute.

A third example of a group of order 16 based on the subgroup $C_4 \times C_2$ is augmented by the relations:

$$C^2 = B \quad AC = CA^3 \quad BC = CB$$

The basis function analysis and full character table are given in appendix 3.3.

Interestingly, first, second and third kind irreducible representations occur.

There are two interlocked four fold cycles based on A^2 :

$$E \quad A \quad A^2 \quad A^3$$

$$E \quad AB \quad A^2 \quad A^3B$$

and four based on B:

$$E \quad C \quad B \quad BC$$

$$E \quad AC \quad B \quad ABC$$

$$E \quad A^2C \quad B \quad A^2BC$$

$$E \quad A^3C \quad B \quad A^3BC$$

and one isolated two fold cycle:

$$E \quad A^2B$$

The elements

$$E \quad A^2 \quad B \quad A^2B$$

constitute separate classes and the remaining elements (all of order four) fall into pairs:

$$(A, A^3) \quad (AB, A^3B) \quad (C, A^2C) \quad (BC, A^2BC) \quad (AC, A^3C) \quad (ABC, A^3BC).$$

It is seen that in the cycles based on A^2 , members of the same cycle fall into the same class, whereas when based on B, members of different cycles are based on the same class.

No representation is faithful so that a four dimensional point group cannot be constructed by doubling the second kind irreducible representation. Further

examination of the character table shows that a four dimensional point group can be formed by adding the following three irreducible representations;

	E	A ²	B	A ² B	2A	2AB	2C	2AC	2BC	2ABC
Γ_{01}	1	1	-1	-1	1	-1	<i>i</i>	<i>i</i>	- <i>i</i>	- <i>i</i>
Γ_{0-1}	1	1	-1	-1	1	-1	- <i>i</i>	- <i>i</i>	<i>i</i>	<i>i</i>
$\Gamma_{(10,-10)}$	2	-2	2	-2	0	0	0	0	0	0

The point group is thus of type $(1d + 1d^*) + 2d$. The orthogonal matrices are listed in the following table, together with their geometrical interpretations.

$$\begin{array}{cccc}
 \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix} \\
 E & A & A^2 & A^3 \\
 C_4(zw) & C_2(zw) & C_4^3(zw) & \\
 \\
 \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix} \\
 B & AB & A^2B & A^3B \\
 C_2(xy) & C_2(xy)C_4(zw) & C_2(xy)C_4^3(zw) & \\
 \\
 \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix} \\
 C & AC & A^2C & A^3C \\
 C_4^3(xy)R(w) & C_4^3(xy)R(\overline{zw}) & C_4^3(xy)R(z) & C_4^3(xy)R(zw) \\
 \cong S_4^3 & \cong S_4^3 & \cong S_4^3 & \cong S_4^3 \\
 \\
 \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & -1 & 0 \end{pmatrix} \\
 BC & ABC & A^2BC & A^3BC \\
 C_4(xy)R(w) & C_4(xy)R(\overline{zw}) & C_4(xy)R(z) & C_4(xy)R(zw) \\
 \cong S_4 & \cong S_4 & \cong S_4 & \cong S_4
 \end{array}$$

The overall picture in this case is relatively straightforward. As in the first example generated from $C_4 \times C_2$, the matrices are separated between the planes xy and zw .

Again the subsets of two dimensional matrices each span two dimensional D_4 with each matrix repeated twice. The detailed pattern is necessarily different and in fact simpler:

- A four-fold cycle based on four-fold rotation in zw (A).
- A four-fold cycle based on two-fold in xy plus four fold in zw (AB).

NOT true.
one (xy)
to (zw)

c) Four S_4 rotation-reflection systems:

Four-fold rotation always in xy plane;

unique reflection line:

$$z \quad w \quad zw \quad \overline{zw}.$$

d) The “four fold inversion” independent of any other cycle.

A final example of a group of order 16 is based on C_8 and is defined by the relations

$$A^8 = E \quad B^2 = E \quad AB = BA^5$$

The basis functions and characters are given in appendix 3.4.

The structure of the group is quite complicated, there being three inter-linked cycles, two of order eight and one of order four as well as two cycles of order two:

$$\begin{array}{ccccccc} A & A^2 & A^3 & A^4 & A^5 & A^6 & A^7 \\ A^3B & A^2 & A^5B & A^4 & A^7B & A^6 & AB \\ & A^2B & & A^4 & & A^6B & \\ & & & B & & & \\ & & & A^4B & & & \end{array}$$

The elements

$$E \quad A^4 \quad A^2 \quad \text{and} \quad A^6$$

fall into separate classes and the remaining elements form classes in pairs:

$$(B, A^4B) \quad (A^2B, A^6B) \quad (A, A^5) \quad (A^3, A^7) \quad (AB, A^5B) \quad (A^3B, A^7B)$$

The two doubly degenerate irreducible representations are both faithful but of the third kind. In this way a four dimensional point group is generated from the sum of the two and is of type $(2d + 2d^*)$. The characters have the values:

	E	A^4	A^2	A^6	2A	$2A^3$	2B	$2A^2B$	2AB	$2A^3B$
$\Gamma_{1,-3}$	2	-2	$2i$	$-2i$	0	0	0	0	0	0
$\Gamma_{-1,3}$	2	-2	$-2i$	$2i$	0	0	0	0	0	0

The particular feature of interest in this point group is that the multiple significance of an operation with repeated eigenvalues $e^{i\theta} e^{-i\theta} e^{i\theta} e^{-i\theta}$ discussed at the end of section 3.2 is illustrated.

The matrix generators for the irreducible representation $\Gamma_{1,3}$ or equivalently $\Gamma_{1,5}$ may be written

$$\begin{pmatrix} \varepsilon_8^1 & 0 \\ 0 & \varepsilon_8^5 \end{pmatrix} \quad \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

$A \qquad B$

so that the full representation may be written in compact form

$$\begin{pmatrix} \varepsilon_8^p & 0 \\ 0 & \varepsilon_8^{5p} \end{pmatrix} \quad \begin{pmatrix} 0 & \varepsilon_8^p \\ \varepsilon_8^{5p} & 0 \end{pmatrix}$$

$A^p \qquad A^p B$

When this is added to its complex conjugate and transformed to real form, the matrices may be written in a similarly compact form:

$$\begin{pmatrix} R_p & 0 \\ 0 & R_{5p} \end{pmatrix} \quad \begin{pmatrix} 0 & R_p \\ R_{5p} & 0 \end{pmatrix}$$

$A^p \qquad A^p B$

In which R_p for example is the 2×2 matrix $\begin{pmatrix} c_p & -s_p \\ s_p & c_p \end{pmatrix}$.

The full set of matrices is

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

E

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \\ 0 & 0 & -1 & 1 \\ 0 & 0 & -1 & -1 \end{pmatrix}$$

A

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

A²

$$\frac{1}{\sqrt{2}} \begin{pmatrix} -1 & -1 & 0 & 0 \\ 1 & -1 & 0 & 0 \\ 0 & 0 & 1 & 1 \\ 0 & 0 & -1 & 1 \end{pmatrix}$$

A³

$$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

A⁴

$$\frac{1}{\sqrt{2}} \begin{pmatrix} -1 & 1 & 0 & 0 \\ -1 & -1 & 0 & 0 \\ 0 & 0 & 1 & -1 \\ 0 & 0 & 1 & 1 \end{pmatrix}$$

A⁵

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$$

A⁶

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & 0 & -1 & -1 \\ 0 & 0 & 1 & -1 \end{pmatrix}$$

A⁷

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

B

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 1 & -1 \\ 0 & 0 & 1 & 1 \\ -1 & 1 & 0 & 0 \\ -1 & -1 & 0 & 0 \end{pmatrix}$$

AB

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

A²B

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & -1 & -1 \\ 0 & 0 & 1 & -1 \\ 1 & 1 & 0 & 0 \\ -1 & 1 & 0 & 0 \end{pmatrix}$$

A³B

$$\begin{pmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}$$

A⁴B

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & -1 & 1 \\ 0 & 0 & -1 & -1 \\ 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \end{pmatrix}$$

A⁵B

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \end{pmatrix}$$

A⁶B

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 1 & 1 \\ 0 & 0 & -1 & 1 \\ -1 & -1 & 0 & 0 \\ 1 & -1 & 0 & 0 \end{pmatrix}$$

A⁷B

All matrices have determinant +1 and therefore all correspond to double rotations. It is recalled that the separate rotation planes are uniquely determined if the rotation angles are different. This is clearly the case for odd powers of A and in the axis system chosen here, they are the xy and the zw planes. The elements $A^p B$ with odd p have the same geometrical significance but their rotation planes are not simply related to the coordinate axes.

The even powers of A have equal double rotation angles so that their rotation planes are not unique: although xy and zw is a possible choice. On the other hand

$$(A^3 B)^2 = A^2$$

so that A^2 would be expected to retain its partial diagonalised form in an axis system which simplified $A^3 B$.

Examination of $A^2 B$ and $A^6 B$ shows that these are double $\pi/2$ rotations and so do not have uniquely defined rotation planes. On the other hand, B and $A^4 B$ are recognised as $\pi, 0$ rotations in planes containing a bisector of x and z and a bisector of y and w.

The two eight fold cycles based on A and $A^3 B$ are clearly geometrically equivalent and a more symmetrical description should result by choosing an axis system related not to A but to the unique pair of elements B and $A^4 B$.

In this way, for generator B

$$\frac{1}{2} \begin{pmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & -1 & 0 \\ 0 & 1 & 0 & -1 \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 1 & 0 & -1 & 0 \\ 0 & 1 & 0 & -1 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

and A becomes

$$\begin{pmatrix} 0 & 0 & 1 & -1 \\ 0 & 0 & 1 & 1 \\ 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \end{pmatrix}$$

The new complete set is then

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

E

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 1 & -1 \\ 0 & 0 & 1 & 1 \\ 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \end{pmatrix}$$

A

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

A²

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & -1 & -1 \\ 0 & 0 & 1 & -1 \\ -1 & -1 & 0 & 0 \\ 1 & -1 & 0 & 0 \end{pmatrix}$$

A³

$$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

A⁴

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & -1 & 1 \\ 0 & 0 & -1 & -1 \\ -1 & 1 & 0 & 0 \\ -1 & -1 & 0 & 0 \end{pmatrix}$$

A⁵

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \end{pmatrix}$$

A⁶

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 1 & 1 \\ 0 & 0 & -1 & 1 \\ 1 & 1 & 0 & 0 \\ -1 & 1 & 0 & 0 \end{pmatrix}$$

A⁷

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

B

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & -1 & 1 \\ 0 & 0 & -1 & -1 \\ 1 & -1 & 0 & 0 \\ 1 & 1 & 0 & 0 \end{pmatrix}$$

AB

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

A²B

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 1 & 1 \\ 0 & 0 & -1 & 1 \\ -1 & -1 & 0 & 0 \\ 1 & -1 & 0 & 0 \end{pmatrix}$$

A³B

$$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

A⁴B

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & 1 & -1 \\ 0 & 0 & 1 & 1 \\ -1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \end{pmatrix}$$

A⁵B

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

A⁶B

$$\frac{1}{\sqrt{2}} \begin{pmatrix} 0 & 0 & -1 & -1 \\ 0 & 0 & 1 & -1 \\ 1 & 1 & 0 & 0 \\ -1 & 1 & 0 & 0 \end{pmatrix}$$

A⁷B

They may be rewritten in the compact form

$$\begin{array}{cccc}
 \begin{pmatrix} R_0 & 0 \\ 0 & R_0 \end{pmatrix} & \begin{pmatrix} R_2 & 0 \\ 0 & R_2 \end{pmatrix} & \begin{pmatrix} R_4 & 0 \\ 0 & R_4 \end{pmatrix} & \begin{pmatrix} R_6 & 0 \\ 0 & R_6 \end{pmatrix} \\
 E & A^2 & A^4 & A^6 \\
 \\
 \begin{pmatrix} 0 & R_1 \\ R_1 & 0 \end{pmatrix} & \begin{pmatrix} 0 & R_3 \\ R_3 & 0 \end{pmatrix} & \begin{pmatrix} 0 & R_5 \\ R_5 & 0 \end{pmatrix} & \begin{pmatrix} 0 & R_7 \\ R_7 & 0 \end{pmatrix} \\
 A & A^3 & A^5 & A^7 \\
 \\
 \begin{pmatrix} R_0 & 0 \\ 0 & R_4 \end{pmatrix} & \begin{pmatrix} R_2 & 0 \\ 0 & R_6 \end{pmatrix} & \begin{pmatrix} R_4 & 0 \\ 0 & R_4 \end{pmatrix} & \begin{pmatrix} R_6 & 0 \\ 0 & R_2 \end{pmatrix} \\
 B & A^2B & A^4B & A^6B \\
 \\
 \begin{pmatrix} 0 & R_5 \\ R_1 & 0 \end{pmatrix} & \begin{pmatrix} 0 & R_7 \\ R_3 & 0 \end{pmatrix} & \begin{pmatrix} 0 & R_1 \\ R_5 & 0 \end{pmatrix} & \begin{pmatrix} 0 & R_3 \\ R_7 & 0 \end{pmatrix} \\
 AB & A^3B & A^5B & A^7B
 \end{array}$$

A full list of four dimensional point groups has not been deduced by the methods emphasised in this thesis. However, the abstract approach has the virtue that a range of examples is generated with relative ease and the orthogonal matrix forms enable the geometrical features to be deduced.

3.8 Concluding Remarks.

In this chapter the problem of point groups generalised to n dimensions has been considered. A simplifying feature is that the elements of such groups can be relatively easily classified in terms of reflection lines and rotation planes no matter how many dimensions are involved. The geometrical elements have been given an algebraic significance by the assignment of orthogonal matrices.

This initial emphasis on algebraic considerations was reinforced when it was found that the basic method developed in chapter two could be extended so that starting from an arbitrary abstract solvable group a group of orthogonal matrices could be generated. It is then possible to give a geometrical description.

Two dimensional and three dimensional point groups are familiar in a number of contexts and in any case are able to be visualised directly. In the case of higher dimensions such visualisation is no longer straightforward. The particular case of four dimensions was discussed in some detail. This involved a new symmetry element the double rotation and it was found that certain geometrical features associated with repeated eigenvalues of the associated orthogonal matrices led to an indefiniteness of the location of the two rotation planes.

It had been hoped to derive a full list of four dimensional point groups but the method as it stands does not readily yield a criterion for such completeness and further work needs to be done in this respect.

APPENDICES.

A3 Groups of Order 16.

Those built up from the maximum invariant subgroup ($C_4 \times C_2$).

$$C_4 \times C_2$$

$$A^4 = B^2 = E \quad AB = BA$$

Symmetry adapted functions are denoted by

$$\Psi_{pq} \quad \begin{array}{l} p = 0, \pm 1, 2 \\ q = 0, 1 \end{array}$$

(A3.1)

To $C_4 \times C_2$ a third element C is added such that

$$C^2 = E \quad AC = CAB \quad BC = CB$$

This group contains two sets of related four-fold cycles;

$$E \quad A \quad A^2 \quad A^3$$

$$E \quad AB \quad A^2 \quad A^3B$$

and

$$E \quad AC \quad A^2B \quad A^3BC$$

$$E \quad A^3C \quad A^2B \quad ABC$$

The effect of C on the symmetry adapted functions of the subgroup is given by

$$C\Psi_{jk} = \Phi_{j+2k, k}$$

There are eight non degenerate basis functions

$$\Psi_{jk} \pm \Phi_{jk} \quad jk = 00, 10, 20, -10$$

and two sets of doubly degenerate basis functions

$$\Psi_{01}, \Phi_{21}$$

$$\Psi_{11}, \Phi_{-11}$$

The class structure is

Class	Order	Class	Order
E	1	A^2B	2
A, AB	4	C, BC	2
A^2	2	AC, ABC	4
A^3, A^3B	4	A^2C, A^2BC	2
B	2	A^3C, A^3BC	4

The character table is

	E	2A	A^2	$2A^3$	B	A^2B	2C	2AC	$2A^2C$	$2A^3C$
Γ_{000}	1	1	1	1	1	1	1	1	1	1
Γ_{001}	1	1	1	1	1	1	-1	-1	-1	-1
Γ_{200}	1	-1	1	-1	1	1	1	-1	1	-1
Γ_{201}	1	-1	1	-1	1	1	-1	1	-1	1
Γ_{100}	1	i	-1	$-i$	1	-1	1	i	-1	$-i$
Γ_{101}	1	i	-1	$-i$	1	-1	-1	$-i$	1	i
Γ_{-100}	1	$-i$	-1	i	1	-1	1	$-i$	-1	i
Γ_{-101}	1	$-i$	-1	i	1	-1	-1	i	1	$-i$
$\Gamma_{01,21}$	2	0	2	0	-2	-2	0	0	0	0
$\Gamma_{11,-11}$	2	0	-2	0	-2	2	0	0	0	0

The generating unitary matrices for the doubly irreducible representation $\Gamma_{01,21}$ are

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}_A \quad \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}_B \quad \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_C$$

and those for $\Gamma_{11,-11}$ are

$$\begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix}_A \quad \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}_B \quad \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}_C$$

The direct sum of the two sets of matrices generates a group of unitary matrices with generators

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & i & 0 \\ 0 & 0 & 0 & -i \end{pmatrix}_A \quad \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}_B \quad \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}_C$$

which can be transformed to real orthogonal form generating a four dimensional point group of type $2d + 2d$. The generating elements of the four dimensional point group are

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix}_A \quad \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}_B \quad \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}_C$$

(A3.2)

To $C_4 \times C_2$ a third element C is added such that

$$C^2 = E \quad AC = CA \quad BC = CA^2B$$

This group also contains four four-fold cycles with the element A^2 in common;

$$E \quad AB \quad A^2 \quad A^3B$$

$$E \quad A \quad A^2 \quad A^3$$

$$E \quad AC \quad A^2 \quad A^3C$$

$$E \quad BC \quad A^2 \quad A^2BC$$

The effect of C on the symmetry adapted functions of the subgroup is

$$C\Psi_{jk} = \Phi_{j+k}$$

There are eight non degenerate basis functions

$$\Psi_{jk} \pm \Phi_{jk} \quad jk = 00, 01, 20, 21$$

and two sets of doubly degenerate basis functions

$$\Psi_{10}, \Phi_{11}$$

$$\Psi_{-10}, \Phi_{-11}$$

and the class structure is;

Class	Order	Class	Order
E	1	AB, A ³ B	4
A	4	C, A ² C	2
A ²	2	AC, A ³ C	4
A ³	4	BC, A ² BC	4
B, A ² B	2	ABC, A ³ BC	2

The character table is

	E	A	A ²	A ³	2B	2AB	2C	2AC	2BC	2ABC
Γ_{000}	1	1	1	1	1	1	1	1	1	1
Γ_{001}	1	1	1	1	1	1	-1	-1	-1	-1
Γ_{010}	1	1	1	1	-1	-1	1	1	-1	-1
Γ_{011}	1	1	1	1	-1	-1	-1	-1	1	1
Γ_{200}	1	-1	1	-1	1	-1	1	-1	1	-1
Γ_{201}	1	-1	1	-1	1	-1	-1	1	-1	1
Γ_{210}	1	-1	1	-1	-1	1	1	-1	-1	1
Γ_{211}	1	-1	1	-1	-1	1	-1	1	1	-1
$\Gamma_{10,11}$	2	2i	-2	-2i	0	0	0	0	0	0
$\Gamma_{-10,-11}$	2	-2i	-2	2i	0	0	0	0	0	0

The non-degenerate irreducible representations are all unfaithful and of the first kind.

The doubly degenerate representations are both third kind. This suggests a point group of type $(2d + 2d^*)$ may be constructed.

The unitary generating matrices for $\Gamma_{10,11}$ are

$$\begin{matrix} \begin{pmatrix} i & 0 \\ 0 & i \end{pmatrix} & \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} & \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \\ A & B & C \end{matrix}$$

A unitary matrix group may be constructed by adding its complex conjugate $\Gamma_{10,11} +$

$\Gamma_{-10,-11}$

$$\begin{matrix} \begin{pmatrix} i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \\ 0 & 0 & -i & 0 \\ 0 & 0 & 0 & -i \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \\ A & B & C \end{matrix}$$

These can be reordered to put complex conjugate elements in adjacent positions

$$\begin{array}{ccc}
 \begin{pmatrix} i & 0 & 0 & 0 \\ 0 & -i & 0 & 0 \\ 0 & 0 & i & 0 \\ 0 & 0 & 0 & -i \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \\
 A & B & C
 \end{array}$$

A transformation to real orthogonal form yields a four dimensional point group with generators

$$\begin{array}{ccc}
 \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} \\
 A & B & C
 \end{array}$$

(A3.3)

To $C_4 \times C_2$ a third element C is added such that

$$C^2 = B \quad BC = CB \quad AC = CA^3$$

This adds four four-fold cycles with the element B in common;

$$E \quad C \quad B \quad BC$$

$$E \quad AC \quad B \quad ABC$$

$$E \quad A^2C \quad B \quad A^2BC$$

$$E \quad A^3C \quad B \quad A^3BC$$

The effect of C on the symmetry adapted functions of $C_4 \times C_2$ is given by

$$C\Psi_{jk} = \Phi_{-jk}$$

$$C^2\Psi_{jk} = \varepsilon_2^k \Psi_{jk}$$

where $j = 0, \pm 1, 2$

and $k = 0, 1$

Thus, there are eight non degenerate basis functions

$$\Psi_{jk} + \varepsilon_4^p \Phi_{jk} \quad jk = 00, 20$$

$$p = 0, 2$$

$$\Psi_{jk} + \varepsilon_4^p \Phi_{jk} \quad jk = 01, 21$$

$$p = +1, -1$$

and two sets of doubly degenerate basis functions

$$\Psi_{10}, \Phi_{-10}$$

$$\Psi_{11}, \Phi_{-11}$$

Thus, the elements of the group are divided into ten different classes:

Class	Order	Class	Order
E	1	AB, A ³ B	4
A, A ³	4	C, A ² C	4
A ²	2	AC, A ³ C	4
B	2	BC, A ² BC	4
A ² B	2	ABC, A ³ BC	4

The character table is

	E	2A	A ²	B	A ² B	2AB	2C	2AC	2BC	2ABC
Γ_{000}	1	1	1	1	1	1	1	1	1	1
Γ_{002}	1	1	1	1	1	1	-1	-1	-1	-1
Γ_{200}	1	-1	1	1	1	-1	1	-1	1	-1
Γ_{202}	1	-1	1	1	1	-1	-1	1	-1	1
Γ_{011}	1	1	1	-1	-1	-1	-i	-i	i	i
Γ_{01-1}	1	1	1	-1	-1	-1	i	i	-i	-i
Γ_{211}	1	-1	1	-1	-1	1	-i	i	i	-i
Γ_{21-1}	1	-1	1	-1	-1	1	i	-i	-i	i
$\Gamma_{10,-10}$	2	0	-2	2	-2	0	0	0	0	0
$\Gamma_{11,-11}$	2	0	-2	-2	2	0	0	0	0	0

This group is of special importance since it contains irreducible representations of the first, second and third kind (all are unfaithful).

A four dimensional point group can be constructed from

$$\Gamma_{011} + \Gamma_{011}^* + \Gamma_{10,-10}$$

i.e. type (1d + 1d^{*}) + 2d.

The unitary generating matrices are

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & i & 0 \\ 0 & 0 & 0 & -i \end{pmatrix}$$

A

$$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

B

$$\begin{pmatrix} -i & 0 & 0 & 0 \\ 0 & i & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

C

with equivalent real forms

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{pmatrix}$$

A

$$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

B

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}$$

C

(A3.4)

$$A^8 = B^2 = E \quad AB = BA^5$$

This group contains two sets of related eight-fold cycles

$$\begin{array}{cccccccc} E & A & A^2 & A^3 & A^4 & A^5 & A^6 & A^7 \\ E & A^3B & A^2 & A^5B & A^4 & A^7B & A^6 & AB \end{array}$$

A four-fold cycle

$$E \quad A^2B \quad A^4 \quad A^6B$$

and two two-fold cycles

$$E \quad B$$

$$E \quad A^4B$$

Symmetry adapted functions of A are denoted

$$\Psi_j \quad \text{where } j = 0, \pm 1, \pm 2, \pm 3, +4$$

The effect of B on Ψ_j is

$$B\Psi_j = \Phi_{5j}$$

j	5j (mod8)
0	0
1	-3
2	2
3	-1
4	4
-3	1
-2	-2
-1	3

The result is eight non degenerate basis functions and two sets of doubly degenerate basis functions.

There are 10 Classes:

$$\begin{array}{cccccc} E & A^4 & A^2 & A^6 & (A, A^5) & (A^3, A^7) & (B, A^4B) \\ & & (A^2B, A^6B) & (AB, A^5B) & (A^3B, A^7B) & & \end{array}$$

The character table is

	E	2A	A ²	2A ³	A ⁴	A ⁶	2B	2AB	2A ² B	2A ³ B
Γ_{00}	1	1	1	1	1	1	1	1	1	1
Γ_{01}	1	1	1	1	1	1	-1	-1	-1	-1
Γ_{20}	1	<i>i</i>	-1	- <i>i</i>	1	-1	1	<i>i</i>	-1	- <i>i</i>
Γ_{21}	1	<i>i</i>	-1	- <i>i</i>	1	-1	-1	- <i>i</i>	1	<i>i</i>
Γ_{-20}	1	- <i>i</i>	-1	<i>i</i>	1	-1	1	- <i>i</i>	-1	<i>i</i>
Γ_{-21}	1	- <i>i</i>	-1	<i>i</i>	1	-1	-1	<i>i</i>	-1	- <i>i</i>
Γ_{40}	1	-1	1	-1	1	1	1	-1	1	-1
Γ_{41}	1	-1	1	-1	1	1	-1	1	-1	1
$\Gamma_{1,3}$	2	0	2 <i>i</i>	0	-2	-2 <i>i</i>	0	0	0	0
$\Gamma_{3,-1}$	2	0	-2 <i>i</i>	0	-2	+2 <i>i</i>	0	0	0	0

The doubly degenerate representations are faithful and of the third kind. A four dimensional point group

$$2d + 2d^*$$

may be constructed.

The unitary generating matrices are

$$\begin{array}{c} \begin{pmatrix} \varepsilon_8^1 & 0 & 0 & 0 \\ 0 & \varepsilon_8^{3*} & 0 & 0 \\ 0 & 0 & \varepsilon_8^3 & 0 \\ 0 & 0 & 0 & \varepsilon_8^{1*} \end{pmatrix} \\ A \end{array} \quad \begin{array}{c} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \\ B \end{array}$$

The matrices may be reordered to put complex conjugate elements in adjacent columns

$$\begin{pmatrix} \varepsilon_8^1 & 0 & 0 & 0 \\ 0 & \varepsilon_8^{1*} & 0 & 0 \\ 0 & 0 & \varepsilon_8^3 & 0 \\ 0 & 0 & 0 & \varepsilon_8^{3*} \end{pmatrix} \quad \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

A B

A transformation to real orthogonal form yields a four dimensional point group with generators

$$\begin{pmatrix} c_1 & -s_1 & 0 & 0 \\ s_1 & c_1 & 0 & 0 \\ 0 & 0 & c_3 & -s_3 \\ 0 & 0 & s_3 & c_3 \end{pmatrix} \quad \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \end{pmatrix}$$

A B

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

A B

CHAPTER FOUR: THE SYMMETRY OF VIBRATIONAL OVERTONES.

4.1. Introduction.

The problem of vibrations [14, 15, 38] in molecules and crystals is particularly well suited to the kind of symmetry analysis developed in this work. In the standard treatment of molecules, the motions of the nuclei are treated under the influence of a potential energy function representing the averaged effect of the electrons. This is the Born-Oppenheimer approximation [39]. Vibrations arise when there is a minimum in the potential energy surface. The potential energy is then expanded in a Taylor series about the minimum. The terms higher than quadratic are first neglected and the problem solved in the corresponding harmonic approximation. The higher terms in the expansion are then reintroduced and their effect determined using perturbation theory: the anharmonic corrections.

The harmonic problem is soluble because it is always possible to find a coordinate transformation which uncouples the potential energy to give a sum of squares. The result is a system of independent harmonic oscillators each with its own characteristic frequency and normal coordinate. It may happen that two or more normal coordinates have the same harmonic frequency and in this case the oscillator is said to be degenerate or isotropic.

In terms of symmetry, the Taylor series belongs to the point or space group corresponding to the nuclear configuration about which the expansion is made. This is the basis for the customary classification of vibrational states in terms of irreducible representations of

point or space groups. A complication arises in the case of an isotropic oscillator. The corresponding operator, which in the harmonic approximation is completely decoupled from the rest of the Hamiltonian, has a much higher symmetry than the point or space group. The resulting energy levels are highly degenerate and for overtones do not correspond to irreducible representations of the underlying point group.

Addition of the anharmonic terms restores the point group symmetry and it is advantageous to adapt the isotropic oscillator functions to this symmetry. This is not a trivial problem and its solution using the symmetry analysis developed in this thesis is the subject of this chapter.

The general features of the harmonic problem are first summarised. The isotropic oscillator is solved both in Cartesian coordinates and in hyperspherical polar coordinates [17]. The latter are found to be the more useful since the angular part of the function both completely determines the symmetry part of the behaviour and is simultaneously an eigenfunction of the square of the total angular momentum generalised to n dimensions. The angular momentum problem is simplified in part by reverting to Cartesian coordinates and in part by making use of a mathematical equivalence of Laplace's equation and the eigenvalue equation for angular momentum [18]. A convenient analysis is developed in terms of homogeneous polynomials a certain subset of which, the harmonic polynomials are solutions of Laplace's equation. In solving the key problem, it is found easiest first to symmetry adapt the homogeneous polynomials and then to construct the harmonic functions.

4.2 The Vibration Problem.

In the vibration problem attention is focused on the motions of the nuclei. The vibrational wave equation is given by

$$H\Psi_v = E_v\Psi_v \quad (4.2.1)$$

The Hamiltonian operator may be written in condensed form

$$H = T_N + V \quad (4.2.2)$$

in which T_N represents the kinetic energy of the nuclei and V is an effective potential energy function which under the Born-Oppenheimer approximation represents an averaged effect of the electrons. In this way the potential energy is a function only of the nuclear coordinates.

Vibrations arise when the nuclei are localised in the region of a particular nuclear configuration and attention may then be focused not on the potential function itself but on a Taylor expansion of the function in powers of suitable coordinates describing displacements from the reference configuration. The form of the Taylor expansion is as follows

$$V = V_0 + \sum_i \left(\frac{\partial V}{\partial q_i} \right)_0 q_i + \frac{1}{2!} \sum_{ij} \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0 q_i q_j + \frac{1}{3!} \sum_{ijk} \left(\frac{\partial^3 V}{\partial q_i \partial q_j \partial q_k} \right)_0 q_i q_j q_k + \dots \quad (4.2.3)$$

The coordinates q_i are convenient displacement coordinates and their value is zero at the reference configuration, indicated by the subscript 0.

The important point is that the Taylor expansion has the symmetry of the reference configuration i.e. the appropriate point or space group. This remains the symmetry group

when the nuclear kinetic energy operators are added to give the total Hamiltonian and the associated vibrational energy levels are classified in terms of the irreducible representations of the corresponding molecular point or crystal space group.

For sufficiently small displacements, cubic and higher terms in the expansion may be neglected and the harmonic approximation is made. Further simplifications are made by choosing the zero of the potential energy to be equal to V_0 and by taking the reference configuration to be at equilibrium so that

$$\left(\frac{\partial V}{\partial q_i} \right)_0 = 0$$

for all q_i . Then the harmonic potential energy has the form

$$V = \frac{1}{2} \sum_{ij} f_{ij} q_i q_j \quad (4.2.4)$$

where

$$f_{ij} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j} \right)_0$$

The order of differentiation is not important so that $f_{ij} = f_{ji}$.

It is well known that the harmonic problem is soluble since it is always possible to find a linear transformation to a set of coordinates (normal coordinates) which eliminates the cross terms in the potential energy [40]. Then

$$V = \frac{1}{2} \sum_j \omega_j^2 Q_j^2$$

and the system is equivalent to a number of independent harmonic oscillators each with its own characteristic frequency ω_j and normal coordinate Q_j .

From the point of view of the present analysis, a complication arises when there is degeneracy: that is when two or more independent normal coordinates correspond to one frequency. The subpart of the problem which deals with degeneracy is called the isotropic oscillator and this has a higher symmetry than the underlying geometrical point or space group leading to higher degeneracies than expected in the corresponding wave functions. This complication disappears when the anharmonic terms are restored to the potential energy. Then, the group of the Hamiltonian is the appropriate geometrical point group. However, resolution into independent coordinates is no longer in general possible and the energy level pattern associated with the isotropic harmonic oscillator is broken down. It is advantageous to adapt the isotropic oscillator functions to the symmetry of the Taylor expansion in order to simplify the analysis when higher order anharmonic terms are restored to the potential energy.

It will be found that the procedure is particularly simple when the underlying group is solvable, as are most three dimensional point groups and all the three dimensional space groups.

In practice, it is usual to label vibrational states in terms of irreducible representations of the underlying point or space group. The ground state and first excited state of a degenerate oscillator are uniquely classifiable in this way. The further excited states (overtones) exhibit the higher degeneracies already referred to and it is these in particular which are simplified by the symmetry adaptation method discussed here.

Attention is concentrated first on the isotropic oscillator problem and the various ways in which its solution may be expressed. It is desirable to maximise the part of the wave

function which is totally symmetric since this will not be affected by any subsequent analysis. It is found that the symmetry sensitive part of the Hamiltonian is equivalent to the square of an angular momentum generalised to a dimension equal to the number of degrees of freedom in the isotropic oscillator.

A requirement then is the generalisation of the familiar treatment of angular momentum in for example the hydrogen atom to an arbitrary number of dimensions.

A key result is the recognition that the eigenvalue equation for the angular momentum squared is equivalent to Laplace's equation. The analysis may be expressed in terms of the homogeneous polynomials, called harmonic polynomials, which are solutions of Laplace's equation and eigenfunctions of the angular momentum. These harmonic polynomials, expressed in Cartesian coordinates, are the exact analogues of the more familiar spherical harmonics in three dimensions in which the angular variables of polar coordinates are used.

As a starting point a brief description of the isotropic oscillator in Cartesian coordinates is given. The complete solution is given in appendix 4.1.

4.3 The Isotropic Oscillator: Solution In Cartesian Coordinates.

The One Dimensional Harmonic Oscillator.

The Hamiltonian operator for a one dimensional harmonic oscillator can be written in simplified form by setting \hbar and ω equal to unity. Then

$$H = \frac{1}{2} \left(Q^2 - \frac{\partial^2}{\partial Q^2} \right) \quad (4.3.1)$$

The eigenvalues are

$$E_n = (n + 1/2) \quad (4.3.2)$$

where the quantum number n can take the values 0, 1, 2, ...

The corresponding non degenerate (unnormalised) eigenfunctions have the form

$$\Psi_n = H_n(Q) \exp[-1/2(Q^2)] \quad (4.3.3)$$

where $H_n(Q)$ is a Hermite polynomial in the coordinate Q . The first few Hermite polynomials are

$$H_0 = 1$$

$$H_1 = 2Q$$

$$H_2 = 4Q^2 - 2$$

$$H_3 = 8Q^3 - 12Q$$

and the rest may be found from the recurrence relation

$$H_{n+1} = 2QH_n - 2nH_{n-1}.$$

In this way, each wave function is the product of a Gaussian times a polynomial in either even or odd powers of the coordinate.

The General d-Dimensional Isotropic Oscillator.

The Hamiltonian for the isotropic oscillator in d-dimensions may be written as an extension of (4.3.1)

$$H = \frac{1}{2} \sum_{j=1}^d \left(Q_j^2 - \frac{\partial^2}{\partial Q_j^2} \right) \quad (4.3.4)$$

It is completely separable in the coordinates Q_j , the solutions then being composed of independent contributions from each constituent one dimensional oscillator. A typical wavefunction is expressed as a product of one dimensional functions, one for each coordinate

$$\Psi_{n_1 n_2 \dots n_d} = \Psi_{n_1}(Q_1) \Psi_{n_2}(Q_2) \dots \Psi_{n_d}(Q_d)$$

and the energy is the a sum of the corresponding one dimensional terms.

$$E_n = \sum_{j=1}^d \left(n_j + \frac{1}{2} d \right) \quad (4.3.5)$$

The energy depends only on the sum of the quantum numbers

$$n = \sum_{j=1}^d n_j$$

so that the energy levels are highly degenerate. A table of degeneracies can be built up.

Table 4.3.1

d	1	2	3	4	5
n					
0	1	1	1	1	1
1	1	2	3	4	5
2	1	3	6	10	15
3	1	4	10	20	35
4	1	5	15	35	70
5	1	6	21	56	126

The table is a rotated form of Pascal's triangle, symmetric with respect to d and $(n+1)$.

The degeneracies are given by

$$c(n, d) = \frac{(n + d - 1)!}{n!(d - 1)!} \quad (4.3.6)$$

From the table it can be seen that for all cases except the one dimensional oscillator, the degeneracy increases with increase of the total quantum number n and tends towards infinity. The underlying group is usually finite and so has only finite order irreducible representations. It follows that the isotropic oscillator functions in general form bases for reducible representations of the point or space group.

The form of a wave function in this coordinate system is thus not symmetry adapted to the underlying symmetry group nor is it readily transformed to symmetry adapted form. An alternative approach is necessary. The isotropic oscillator problem is separable in both Cartesian and polar coordinates. The polar coordinate form will now be examined.

4.4 The Isotropic Oscillator: Solution In Hyperspherical Polar Coordinates.

4.4.1 Transformation to hyperspherical polar coordinates.

The potential energy depends on only a single variable

$$r_{(d)} = \left(\sum_{j=1}^d Q_j^2 \right)^{\frac{1}{2}} \quad (4.4.1)$$

which may be identified as the radial coordinate in the hyperspherical polar coordinate system. The kinetic energy operator is proportional to the Laplacian operator which in polar coordinates has the form [18]

$$\sum_{j=1}^d \left(\frac{\partial^2}{\partial Q_j^2} \right) \equiv \Delta_{(d)} = \left(\frac{\partial^2}{\partial r^2} \right) + \frac{(d-1)}{r} \left(\frac{\partial}{\partial r} \right) - \frac{M_{(d)}^2}{r^2} \quad (4.4.2)$$

All the angular factors are gathered in the term $M_{(d)}^2$, which is the square of a generalised angular momentum. This may be defined as a sum of squares of components, one for each pair of Cartesian axes corresponding to the possible planes of rotation.

$$M_{(d)}^2 = \sum_{i=1}^{d-1} \sum_{j=i+1}^d M_{ij}^2 \quad (4.4.3)$$

where

$$M_{ij} = -i \left(Q_i \frac{\partial}{\partial Q_j} - Q_j \frac{\partial}{\partial Q_i} \right) \quad (4.4.4)$$

An eigenfunction of the Hamiltonian in hyperspherical coordinates can be written as the product of a radial factor and an eigenfunction of the angular momentum squared. For the

symmetry problem, it is only the angular momentum part which is important and it is this part of the solution to which attention is presently confined.

It is characteristic of the analysis developed here that the angular part once identified is recast in terms of Cartesian coordinates which are much easier to handle.

In order to understand the composition of the angular momentum functions a brief description of homogeneous and harmonic polynomials will be given in the next section.

4.4.2 Homogeneous Polynomials, Harmonic Polynomials and Angular Momentum.

Homogeneous polynomials in the x coordinates, i.e. polynomials in which the total power of each separate product of coordinates is the same, will be denoted by the symbol f . They satisfy the Euler relation

$$\sum_{j=1}^d x_j \frac{\partial f_\lambda}{\partial x_j} = \lambda f_\lambda$$

The subscript λ denotes the total power or order of the polynomial.

The number of independent polynomials is equal to the number of distinct single products which can be formed for a particular order λ and dimension d . It is readily shown that the value is

$$c(\lambda, d) = \frac{(\lambda + d - 1)!}{\lambda!(d - 1)!} \quad (4.4.5)$$

and so is equal to the degeneracy of the corresponding isotropic oscillator state for $n = \lambda$ (4.3.6).

A subset of homogeneous polynomials in addition satisfy Laplace's equation. Such a polynomial is called harmonic and will be denoted by h .

$$\Delta h_\lambda = 0 \quad (4.4.6)$$

The subscript λ , as before, indicates the order of the polynomial.

Any function h which satisfies (6) for a particular value of d is also a solution for all higher values of the dimensionality.

Polar coordinates can be built up in d -dimensions.

$$\begin{aligned}
\text{For } d = 2 \quad x_1 &= r_2 \cos \phi \\
x_2 &= r_2 \sin \phi \quad \phi = 0 \text{ to } 2\pi \\
\text{For } d = 3 \quad x_1 &= r_3 \sin \theta_3 \cos \phi \\
x_2 &= r_3 \sin \theta_3 \sin \phi \\
x_3 &= r_3 \cos \theta_3 \quad \theta_3 = 0 \text{ to } \pi \quad (4.4.7) \\
\text{For } d = 4 \quad x_1 &= r_4 \sin \theta_4 \sin \theta_3 \cos \phi \\
x_2 &= r_4 \sin \theta_4 \sin \theta_3 \sin \phi \\
x_3 &= r_4 \sin \theta_4 \cos \theta_3 \\
x_4 &= r_4 \cos \theta_4 \quad \theta_4 = 0 \text{ to } \pi
\end{aligned}$$

It is apparent that each additional dimension has the same form i.e. $x_d = r_d \cos \theta_d$ and that no matter what the dimensionality is the coordinates remain linear with respect to the radial distance. The polar coordinate system corresponds to a radial distance r_d and $(d-1)$ angles. Hence in polar coordinates a harmonic polynomial can be expressed as the product

$$h_\lambda = r^\lambda \Omega \quad (4.4.8)$$

where Ω is a function only of the angular variables and the homogeneity appears in the radial part.

When the Laplacian operator is written in polar coordinates, as in (2), and allowed to operate on the harmonic polynomial (8),

$$\left[\left(\frac{\partial^2}{\partial r^2} \right) + \frac{(d-1)}{r} \left(\frac{\partial}{\partial r} \right) - \frac{M^2}{r^2} \right] r^\lambda \Omega = 0 \quad (4.4.9)$$

the result may be written

$$M^2(r^\lambda \Omega) = \lambda(\lambda + d - 2)(r^\lambda \Omega) \quad (4.4.10)$$

In this way, finding a homogeneous polynomial of order λ which satisfies Laplace's equation in d -dimensions is equivalent to finding an eigenfunction of the corresponding angular momentum squared with eigenvalue $\lambda(\lambda+d-2)$ [18].

Correspondingly, a homogeneous polynomial which is an eigenfunction of M^2 for a particular dimensionality remains an eigenfunction for all higher dimensionalities with a suitably modified eigenvalue. This property enables a complete set of independent harmonic polynomials to be built up from the solutions for two and three dimensions, well known in other contexts, by a process of induction. The building up procedure is outlined in the following section.

4.4.3 Derivation of Harmonic Polynomials.

The eigenfunctions of M^2 are well known in two and three dimensions. In order to construct a method by which the eigenfunctions of M^2 , that is to say the harmonic polynomials, can be determined in any number of dimensions we begin by reviewing the commutation properties of angular momentum operators M_{ij} defined by equation (4).

Their commutation relations are

$$[M_{ij}, M_{kl}] = 0 \text{ if all four indices are different}$$

$$[M_{ik}, M_{jk}] = iM_{ij} \text{ if } i, j \text{ and } k \text{ are different.}$$

The square of the angular momentum operators may be built up as follows:

$$M_{(2)}^2 = M_{12}^2$$

$$M_{(3)}^2 = M_{(2)}^2 + M_{13}^2 + M_{23}^2$$

$$M_{(4)}^2 = M_{(3)}^2 + M_{14}^2 + M_{24}^2 + M_{34}^2 \quad \text{etc.}$$

Examination of the commutation relations between these operators leads to the conclusion that

$$M_{(2)}^2, M_{(3)}^2, M_{(4)}^2, \dots, M_{(d)}^2$$

form a set of commuting operators. It follows that the eigenfunctions of $M_{(d)}^2$ can be chosen to be simultaneous eigenfunctions of $M_{(2)}^2, M_{(3)}^2, \dots$ and $M_{(d-1)}^2$.

In polar coordinate terms (7)

eigenfunctions of $M_{(2)}^2$ are functions of ϕ

eigenfunctions of $M_{(3)}^2$ are functions of ϕ and $\theta_{(3)}$

eigenfunctions of $M_{(4)}^2$ are functions of $\phi, \theta_{(3)}$ and $\theta_{(4)}$

etc. Therefore, an eigenfunction can be written as a product

$$f(\phi)g(\theta_{(3)})h(\theta_{(4)})\dots$$

In two dimensions, it is usual to label the states by a quantum number m which takes values $0, \pm 1, \pm 2 \dots$. This corresponds to the fact that there are two harmonic polynomials for all non zero values of m .

In three dimensions, it is well known that a second quantum number is added

$$l_3 = 0, 1, 2, \dots$$

and that each has $(2l + 1)$ associated values of m

$$m = l_3, l_3 - 1, \dots, -l_3.$$

The limitation arises because the value of $M_{(3)}^2$ must be greater than or equal to the value of the square of any one of its components.

When a fourth dimension is added, the new quantum number behaves like l_3

(corresponding to the addition of the coordinate θ_4 , the angle between $r_{(4)}$ and the new Cartesian axis). In this way

$$l_4 = 0, 1, 2, \dots$$

$$l_3 = 0, 1, 2, \dots, l_4 - 1.$$

All higher dimensions add a similar pair of conditions.

In two dimensions, there is only one factor in the square of the angular momentum, so that attention may be directed towards the angular momentum itself (see appendix 4.2). In the usual notation

$$M_z = -i \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

The solutions of M_z are well known. Ignoring normalisation

$$\Psi_m = \exp(im\phi)$$

where it is recalled that $m = 0, \pm 1, \pm 2, \dots$

When multiplied by $r^{|m|}$ these give the harmonic polynomials, there being one harmonic polynomial for $m = 0$ and two polynomials for all higher values. It is sometimes convenient to replace the set by the real and imaginary parts which can be seen to have the form for $m \neq 0$

$$r^{|m|} \cos m\phi \quad \text{and} \quad r^{|m|} \sin m\phi$$

where m is now restricted to positive values.

In Cartesian form the solutions can be summarised in a table, the label λ being employed to connect with the notation used for harmonic polynomials.

$\lambda (\equiv m)$	h_λ	
0	1	
1	x	y
2	$x^2 - y^2$	$2xy$
3	$x^3 - 3xy^2$	$3x^2y - y^3$

In three dimensions

$$M_{(3)}^2 = M_x^2 + M_y^2 + M_z^2$$

Eigenfunctions of $M_{(3)}^2$ are functions of two polar coordinates ϕ and $\theta_{(3)}$ i.e.

$$\Psi(\theta_3, \phi) = f(\theta_3)f(\phi)$$

which implies that the harmonic polynomials which are solutions of $M_{(3)}^2$ can be written in the form

$$h_{l_3}(xyz) = h_m(xy)f(\theta_3)$$

where $l_3 = 0, 1, 2, \dots$

$m = l_3, l_3-1, \dots -l_3$.

For the θ_3 part, $f(\theta_3)$ is strictly $f(\cos\theta_3)$ for which we know $\cos\theta_3 = z/r_{(3)}$ and hence, a polynomial in $\cos\theta$ is essentially a homogeneous polynomial in z and $r_{(3)}^2$ or equivalently z and $r_{(2)}^2$ since $r_{(3)}^2 = (x^2 + y^2 + z^2) = r_{(2)}^2 + z^2$. This gives

$$h_{l_3}(xyz) = h_m(xy)f_{l_3-m}(z, r_{(2)}^2)$$

In effect the θ part of the solution can be expressed as powers of z multiplied by even powers of r to form polynomials of the kind

$$az^2 + br_{(2)}^2$$

$$az^3 + bzr_{(2)}^2$$

$$az^4 + bz^2r_{(2)}^2 + cr_{(2)}^4$$

etc. The coefficients of the expansion in $f(z, r_{(2)}^2)$ can be found from the condition that h_{l_3}

satisfies Laplace's equation:

$$\Delta_{(3)} h_{l_3}(xyz) = 0$$

A simplification is that a solution in two dimensions remains a solution in all higher dimensions. The additional three dimensional solutions are given in the following table:

$\lambda(\equiv l_3)$	h_λ
0	1
1	z
2	$2z^2-x^2-y^2$ xz yz
3	$z(2z^2-3x^2-3y^2)$ $x(4z^2-x^2-y^2)$ $y(4z^2-x^2-y^2)$ $z(x^2-y^2)$ $2xyz$

This method is readily extended to higher dimensions so that for example

$$\begin{aligned}
 h_{l_4}(xyzw) &= h_m(xy) f_{l_3-m}(z, r_{(2)}^2) f_{l_4-l_3}(w, r_{(3)}^2) \\
 &= h_{l_3}(xyz) f_{l_4-l_3}(w, r_{(3)}^2)
 \end{aligned}$$

Now, $f_{l_4-l_3}$ is a homogeneous polynomial in w and $r_{(3)}^2$

$$f_{l_4-l_3} = f_\kappa = aw^\kappa + bw^{\kappa-2}r_{(3)}^2 + cw^{\kappa-4}r_{(3)}^4 + \dots$$

Again, solutions in lower dimensions remain solutions in higher dimensions and the

following table lists only the additional four dimensional solutions:

$\lambda(\equiv l_4)$	h_λ
0	1
1	w
2	xw yw zw $3w^2-(x^2+y^2+z^2)$
3	$w(w^2-x^2-y^2-z^2)$ $x(5w^2-x^2-y^2-z^2)$ $y(5w^2-x^2-y^2-z^2)$ $z(5w^2-x^2-y^2-z^2)$ $w(x^2-y^2)$ $2xyw$ $w(2z^2-x^2-y^2)$ xzw yzw

Using these results it is possible to construct a table giving the degeneracies of the values of angular momentum squared as a function of quantum number and dimensionality.

Table 4.4.1

d	2	3	4	5
λ				
0	1	1	1	1
1	2	3	4	5
2	2	5	9	14
3	2	7	16	30
4	2	9	25	55
5	2	11	36	91

The values may be compared with the table of degeneracies of the isotropic oscillator. It will be seen that above $\lambda = 1$ the degeneracies of the angular functions are less than the degeneracies of the isotropic oscillator functions. Thus, the energy levels of the isotropic oscillator cannot be labeled by a single value of angular momentum. Closer examination shows that the oscillator degeneracy is the sum of the angular momentum degeneracy for $\lambda = n$ plus all lower odd or even values of λ as appropriate.

In order to complete the solution of the isotropic oscillator the radial dependent terms must be included. The function

$$h_{\lambda} \exp\left(-\frac{1}{2} r_{(d)}^2\right)$$

can be shown to be an eigenfunction of H with eigenvalue $\lambda + (1/2)d$. The other solutions have the form

$$\left(\text{polynomial in } r_{(d)}^2\right) h_{\lambda} \exp\left(-\frac{1}{2} r_{(d)}^2\right)$$

such as

$$\left(1 + ar_{(d)}^2\right) h_{\lambda} \exp\left(-\frac{1}{2} r_{(d)}^2\right).$$

4.5 Solvable Groups and the Isotropic Oscillator.

The solvable group treatment developed in chapter two leads to the construction of a complete set of symmetry adapted functions generated from a single arbitrary function.

In the problem of molecular vibrations the solvable group is the group of the Taylor expansion of the potential energy.

For use in the present application, the key feature of the symmetry adapted set is the operator equation

$$A\phi_j = \epsilon_{jk}\phi_k \quad (4.5.1)$$

In this way the set $\phi_1, \phi_2, \dots, \phi_n$ forms a basis for an n-fold degenerate irreducible representation and the effect of any symmetry operator A on one of the functions is to give one other member of the set only (with the possibility that $j = k$) multiplied by a root of unity.

This result makes it particularly easy to determine the symmetry behavior of powers of the original functions, which may then themselves be symmetry adapted using the basic procedure.

The ground state function of the isotropic oscillator is

$$\exp\left(-\frac{1}{2}r_{(d)}^2\right)$$

which is totally symmetric and no further analysis is necessary.

The first excited state is n-fold degenerate, the functions having the form

$$Q_j \exp\left(-\frac{1}{2}r_{(d)}^2\right) \quad j = 1, 2, \dots, n$$

The exponential factor is totally symmetric so that for the purpose of this analysis, the set is

Q_1, Q_2, \dots, Q_n

i.e. the set of normal coordinates itself.

The effect of the group operators on the Q coordinates exactly parallels (1)

$$AQ_j = \epsilon_{jk} Q_k \quad (4.5.2)$$

For powers of the Q coordinates, the effect of the symmetry operators follows at once from (2). For example

$$AQ_j^2 = (\epsilon_{jk})^2 Q_k^2$$

$$AQ_j Q_{j'} = \epsilon_{jk} \epsilon_{j'k'} Q_k Q_{k'}$$

Analysis of these product functions will lead to a symmetry adaptation of the whole set of homogeneous polynomials of a given order. The basic equation (1) ensures that the set is subdivided, since for example Q_1^3 can only be combined with Q_2^3, Q_3^3, \dots , and $Q_1^2 Q_2$ with $Q_1 Q_2^2, Q_1^2 Q_3, \dots$. In this way it is each subset which is symmetry adapted.

In this application, harmonic polynomials are required, which are eigenfunctions of the angular momentum and this connects with the symmetry determining part of the vibrational wave function. These may be obtained by forming linear combinations of homogeneous polynomials of the same symmetry type which satisfy Laplace's equation.

The development of the method is best illustrated by means of examples.

4.6 The Symmetry Of Molecular Overtones.

4.6.1 Analysis of doubly degenerate vibrations.

As an example of a molecule possessing a doubly degenerate vibration the dihedral group D_3 will be considered.

Properties of the group were worked out in chapter two.

The character table for the group D_3 is

D_3		E	2A	3B
Γ_{00}	(A_1)	1	1	1
Γ_{01}	(A_2)	1	1	-1
$\Gamma_{1,-1}$	(E)	2	-1	0

The table includes the familiar Schönflies notation for the irreducible representations and this will be used in what follows to emphasise the relevance to vibrational overtones.

Let us consider the basis functions for the doubly degenerate representation (E) in more detail.

It is the deformation coordinate functions which are of interest. These are taken to be real, so that the symmetry adapted combinations satisfy

$$\Psi_{-j} = \Psi_j^*$$

where * indicates complex conjugate.

It is recalled that the treatment leads to two pairs of doubly degenerate functions

$$\begin{array}{l} \Psi_1 \text{ with } \phi_{-1} \text{ and} \\ \phi_1 \text{ with } \Psi_{-1} \end{array}$$

in terms of complex conjugates these may be rewritten:

$$\begin{array}{l} \Psi_1 \text{ with } \phi_1^* \text{ and} \\ \phi_1 \text{ with } \Psi_1^* \end{array}$$

In this way, the degenerate pairs are not in general complex conjugate pairs. In the problem under consideration, the symmetry adapted functions would correspond to normal coordinate functions of the vibrating system. Since these arise from a Hermitian eigenvalue problem, complex normal coordinates corresponding to a two dimensional oscillator must be a pair of complex conjugates. The pair of functions spanning the doubly degenerate representation must therefore be converted to a pair of complex conjugates by the transformation:

$$\begin{array}{ll} \frac{1}{\sqrt{2}} \{ \Psi_1 + \phi_1 \} & \frac{1}{\sqrt{2}} \{ \phi_1^* + \Psi_1^* \} \\ \frac{-i}{\sqrt{2}} \{ \Psi_1 - \phi_1 \} & \frac{-i}{\sqrt{2}} \{ \phi_1^* - \Psi_1^* \} \end{array}$$

For simplicity, the pair of complex conjugate normal coordinates will be denoted by Q_+ and Q_- . The effects of the group operations on these coordinates can be summarised as follows

	E	A	A ²	B	AB	A ² B
Q ₊	Q ₊	ωQ_+	$\omega^* Q_+$	Q ₋	$\omega^* Q_-$	ωQ_-
Q ₋	Q ₋	$\omega^* Q_-$	ωQ_-	Q ₊	ωQ_+	$\omega^* Q_+$

The standard procedure for determining symmetry adapted overtone functions, described in the preceding sections, leads first to symmetry adapted homogeneous polynomials which are then converted to harmonic polynomials which conserve the symmetry properties. In this example, it will be found that the symmetry adapted homogeneous polynomials already contain the harmonic polynomials as an identifiable subset.

Harmonic polynomials are solutions of Laplace's equation. In two dimensions, this is usually written

$$\Delta\phi = \left\{ \frac{\partial^2}{\partial Q_1^2} + \frac{\partial^2}{\partial Q_2^2} \right\} \phi = 0$$

This form refers to real variables. If replaced by a complex conjugate pair, for example Q_+ and Q_- in the present case, Laplace's equation becomes

$$\Delta\phi = 2 \left\{ \frac{\partial^2}{\partial Q_+ \partial Q_-} \right\} \phi = 0$$

The harmonic polynomials are therefore either powers of Q_+ only or powers of Q_- only and it is only these which need to be considered in the symmetry analysis. As a confirmation of this result, it is noted that when expressed in terms of their real and imaginary parts, x and y say, powers of the complex coordinates take the form

$$Q_{\pm}^{\lambda} = (x \pm iy)^{\lambda} = r^{\lambda} \exp(\pm i\lambda\varphi)$$

i.e. the eigenfunctions of two dimensional angular momentum in more familiar form.

From the table of operator effects, it is seen that

$$AQ_{\pm} = \varepsilon_3^{\pm 1} Q_{\pm}$$

so that

$$AQ_{\pm}^m = \varepsilon_3^{\pm\mu} Q_{\pm}^m$$

where $\mu = m \bmod 3$. There are just three distinct values of μ which may be chosen as 0, ± 1 . The values of μ in effect give a classification of the functions with respect to the three fold axis. In this way

m	μ for Q_+^m	μ for Q_-^m
1	1	-1
2	-1	1
3	0	0
4	1	-1

and so on through a three fold cycle.

The operator B interchanges the two functions:

$$BQ_{\pm}^m = Q_{\mp}^m$$

If three is a factor of m, the two functions may be combined to give simultaneous eigenfunctions of A and B. In terms of the familiar Schönflies notation

$$Q_+^{3m} + Q_-^{3m} \text{ transforms like irreducible representation } A_1$$

$$Q_+^{3m} - Q_-^{3m} \text{ transforms like irreducible representation } A_2.$$

If m is not divisible by three, simultaneous eigenfunctions cannot be constructed and the pair of functions are irreducible and of type E.

The symmetry adapted functions and the irreducible representations Γ to which they may belong are summarised as follows.

Table 4.6.1

m	Functions	Symmetry
0	1	A_1
1	(Q_+, Q_-)	E
2	(Q_-^2, Q_+^2)	E
3	$Q_+^3 + Q_-^3$	A_1
	$Q_+^3 - Q_-^3$	A_2
4	Q_+^4, Q_-^4	E
5	Q_-^5, Q_+^5	E

Again, a three fold cycle is followed. For the E functions, the first member of the pair goes with $\mu = 1$ and the second with $\mu = -1$.

The results enable the pattern of overtone symmetries to be written down, since for each value of the vibrational quantum number n , there are angular momentum components with $m = n, n-2, \dots$ (see appendix 4.2). In this way

$n = 0$	$m = 0$	A_1
$n = 1$	$m = 1$	E
$n = 2$	$m = 0$	A_1
	$m = 2$	E
$n = 3$	$m = 3$	$A_1 + A_2$
	$m = 1$	E

$n = 4$	$m = 4$	E
	$m = 2$	E
	$m = 0$	A_1

etc.

The angular momentum parts of the wave functions in the form of harmonic polynomials are given in the previous table.

The analysis has been given in detail because in all molecular point groups (and all three dimensional space groups) doubly degenerate representations can be treated in the same basic way. The generalisation to C_{nv} (and the isomorphic D_n) groups is fairly obvious with an n -fold cycle replacing the previous three fold cycle. In the case of tetrahedral and octahedral groups, the doubly degenerate representations are associated with the four three-fold axes acting in concert and so the analysis is essentially similar to that for C_{3v} . Icosahedral groups have no two dimensional irreducible representations.

4.6.2 Analysis of triply degenerate vibrations.

It was found in the previous treatment that a doubly degenerate vibration constituted a special case of the more general treatment. A triply degenerate vibration provides a more typical example and the case of A_4 (corresponding to the three dimensional point group T) is now considered in detail.

It is recalled that the simplifications associated with a solvable group may be traced to the equation representing the effect of a group operator on one of the basis functions underlying an irreducible representation. Consider a representation of dimension n with basis functions

$$\phi_1, \phi_2, \dots \phi_n.$$

The effect of an operator A on any one of the basis functions ϕ_j is given by

$$A\phi_j = \epsilon_{jk}\phi_k$$

i.e. the function is transformed into one other basis function (possibly itself) times a root of unity.

It is possible to construct tables which provide all possible relations for sample basis functions for each of the irreducible representations.

The properties of the group A_4 were derived in detail in section 2.7.2.

The character table of irreducible representations is

		E	3A	4C	4C ²
Γ_{000}	(A)	1	1	1	1
Γ_{001}	(E ⁺)	1	1	ω	ω^*
Γ_{00-1}	(E ⁻)	1	1	ω^*	ω
$\Gamma_{10,01,11}$	(T)	3	-1	0	0

The familiar Schönflies notation has been added to facilitate comparison with analysis of molecular vibrations. The separate complex conjugate one dimensional irreducible representations are distinguished by a superscript.

A table of all possible equations of type (1) is presented.

Table 4.6.2

	ϕ_0 (A)	ϕ_1 (E^+)	ϕ_{-1} (E^-)	ϕ_{10} (T)	ϕ_{01} (T)	ϕ_{11} (T)
E	ϕ_0	ϕ_1	ϕ_{-1}	ϕ_{10}	ϕ_{01}	ϕ_{11}
A	ϕ_0	ϕ_1	ϕ_{-1}	$-\phi_{10}$	ϕ_{01}	$-\phi_{11}$
B	ϕ_0	ϕ_1	ϕ_{-1}	ϕ_{10}	$-\phi_{01}$	$-\phi_{11}$
AB	ϕ_0	ϕ_1	ϕ_{-1}	$-\phi_{10}$	$-\phi_{01}$	ϕ_{11}
C	ϕ_0	$\omega\phi_1$	$\omega^*\phi_{-1}$	ϕ_{01}	ϕ_{11}	ϕ_{10}
AC	ϕ_0	$\omega\phi_1$	$\omega^*\phi_{-1}$	ϕ_{01}	$-\phi_{11}$	$-\phi_{10}$
BC	ϕ_0	$\omega\phi_1$	$\omega^*\phi_{-1}$	$-\phi_{01}$	$-\phi_{11}$	ϕ_{10}
ABC	ϕ_0	$\omega\phi_1$	$\omega^*\phi_{-1}$	$-\phi_{01}$	ϕ_{11}	$-\phi_{10}$
C^2	ϕ_0	$\omega^*\phi_1$	$\omega\phi_{-1}$	ϕ_{11}	ϕ_{10}	ϕ_{01}
AC^2	ϕ_0	$\omega^*\phi_1$	$\omega\phi_{-1}$	$-\phi_{11}$	$-\phi_{10}$	ϕ_{01}
BC^2	ϕ_0	$\omega^*\phi_1$	$\omega\phi_{-1}$	$-\phi_{11}$	ϕ_{10}	$-\phi_{01}$
ABC^2	ϕ_0	$\omega^*\phi_1$	$\omega\phi_{-1}$	ϕ_{11}	$-\phi_{10}$	$-\phi_{01}$

In the present context it is the triply degenerate vibration of type T which is of interest and in particular the symmetry adapted forms of the overtones. The first part of the analysis adapts the whole set of homogeneous polynomials in the normal coordinate functions Q_{10} , Q_{01} , Q_{11} which transform like ϕ_{10} , ϕ_{01} , ϕ_{11} .

For $n = 0$, the only polynomial is 1 which is clearly totally symmetric and corresponds to the irreducible representation A.

For $n = 1$, the polynomials are the normal coordinate functions themselves and are of type T.

For $n = 2$ consider Q_{10}^2 . Then from the basic table

$$XQ_{10}^2 = Q_{10}^2 \quad XQ_{01}^2 = Q_{01}^2 \quad XQ_{11}^2 = Q_{11}^2$$

where X is composed of A and B only.

The functions are totally symmetric under $C_2 \times C_2$ and may be combined to give eigenfunctions of C and C^2

$$Q_{10}^2 + Q_{01}^2 + Q_{11}^2 \quad \text{Type A}$$

$$Q_{10}^2 + \omega Q_{01}^2 + \omega^* Q_{11}^2 \quad \text{Type E}^+$$

$$Q_{10}^2 + \omega^* Q_{01}^2 + \omega Q_{11}^2 \quad \text{Type E}^-$$

For the set of cross terms, it is easily deduced that

$Q_{10}Q_{01}$ transform like Q_{11} and so the set forms a basis for representation T:

$$(Q_{01}Q_{11}; Q_{11}Q_{10}; Q_{10}Q_{01})$$

Proceeding to cubic terms, it is clear that Q_{10}^3 transforms like Q_{10} and the set

$$(Q_{10}^3; Q_{01}^3; Q_{11}^3)$$

again form a basis for T.

The function $Q_{11}^2 Q_{01}$ behaves like Q_{01} and so two more sets of T functions can be found:

$$(Q_{01}^2 Q_{10}; Q_{11}^2 Q_{01}; Q_{10}^2 Q_{11})$$

$$(Q_{11}^2 Q_{10}; Q_{10}^2 Q_{01}; Q_{01}^2 Q_{11})$$

Finally the single function $(Q_{10} Q_{01} Q_{11})$ forms a basis for A.

Proceeding in this way it is straight forward to deduce the list of homogeneous polynomials symmetry adapted to T. They are collected in the following table.

Table 4.6.3

n	Homogeneous polynomial	Symmetry
n = 0	1	A
n = 1	(Q_{10} ; Q_{01} ; Q_{11})	T
n = 2	$Q_{10}^2 + Q_{01}^2 + Q_{11}^2$	A
	$Q_{10}^2 + \omega Q_{01}^2 + \omega^* Q_{11}^2$	E^+
	$Q_{10}^2 + \omega^* Q_{01}^2 + \omega Q_{11}^2$	E^-
	($Q_{01}Q_{11}$; $Q_{11}Q_{10}$; $Q_{10}Q_{01}$)	T
n = 3	(Q_{10}^3 ; Q_{01}^3 ; Q_{11}^3)	T
	($Q_{01}^2Q_{10}$; $Q_{11}^2Q_{01}$; $Q_{10}^2Q_{11}$)	T
	($Q_{11}^2Q_{10}$; $Q_{10}^2Q_{01}$; $Q_{01}^2Q_{11}$)	T
	$Q_{10}Q_{01}Q_{11}$	A
n = 4	$Q_{10}^4 + Q_{01}^4 + Q_{11}^4$	A
	$Q_{10}^4 + \omega Q_{01}^4 + \omega^* Q_{11}^4$	E^+
	$Q_{10}^4 + \omega^* Q_{01}^4 + \omega Q_{11}^4$	E^-
	($Q_{01}^3Q_{11}$; $Q_{11}^3Q_{10}$; $Q_{10}^3Q_{01}$)	T
	($Q_{01}Q_{11}^3$; $Q_{11}Q_{10}^3$; $Q_{10}Q_{01}^3$)	T
	$Q_{01}^2Q_{11}^2 + Q_{11}^2Q_{10}^2 + Q_{10}^2Q_{01}^2$	A
	$Q_{01}^2Q_{11}^2 + \omega Q_{11}^2Q_{10}^2 + \omega^* Q_{10}^2Q_{01}^2$	E^+
	$Q_{01}^2Q_{11}^2 + \omega^* Q_{11}^2Q_{10}^2 + \omega Q_{10}^2Q_{01}^2$	E^-
	$Q_{10}^2Q_{01}Q_{11}$; $Q_{10}Q_{01}^2Q_{11}$; $Q_{10}Q_{01}Q_{11}^2$	T

$n = 5$	$(Q_{10}^5; Q_{01}^5; Q_{11}^5)$	T
	$(Q_{01}^4 Q_{10}; Q_{11}^4 Q_{01}; Q_{10}^4 Q_{11})$	T
	$(Q_{11}^4 Q_{10}; Q_{10}^4 Q_{01}; Q_{01}^4 Q_{11})$	T
	$(Q_{01}^2 Q_{10}^3; Q_{11}^2 Q_{01}^3; Q_{10}^2 Q_{11}^3)$	T
	$(Q_{11}^2 Q_{10}^3; Q_{10}^2 Q_{01}^3; Q_{01}^2 Q_{11}^3)$	T
	$(Q_{01}^2 Q_{11}^2 Q_{10}; Q_{11}^2 Q_{10}^2 Q_{01}; Q_{10}^2 Q_{01}^2 Q_{11})$	T
	$Q_{10}^3 Q_{01} Q_{11} + Q_{10} Q_{01}^3 Q_{11} + Q_{10} Q_{01} Q_{11}^3$	A
	$Q_{10}^3 Q_{01} Q_{11} + \omega Q_{10} Q_{01}^3 Q_{11} + \omega^* Q_{10} Q_{01} Q_{11}^3$	E^+
	$Q_{10}^3 Q_{01} Q_{11} + \omega^* Q_{10} Q_{01}^3 Q_{11} + \omega Q_{10} Q_{01} Q_{11}^3$	E^-

The procedure whereby the homogeneous polynomials are reduced to the set of harmonic polynomials while maintaining the property of symmetry adaptation to the underlying group is now addressed.

For $n = 0$, the A function 1 is harmonic, with angular momentum quantum number $\lambda = 0$.

For $n = 1$, the set of T functions is also harmonic and corresponds to $\lambda = 1$.

When $n = 2$, the set of six functions covers two values of the angular momentum $\lambda = 0$ and 2. It is already known that $\lambda = 0$ has symmetry A. The single function belonging to $n = 2$ and symmetry A is therefore not harmonic as can be checked by verifying that it is not annihilated by the Laplacian operator. The remaining five functions of symmetry E^+ , E^- and T are therefore harmonic and this can be confirmed by applying the Laplacian.

Proceeding to $n = 3$, angular momentum components of $\lambda = 1$ and 3 are included. For the $\lambda = 1$, it has been shown that its symmetry is T. The $n = 3$ basis includes 3 sets of T symmetry. Combinations of the three polynomials of the same symmetry types are sought which satisfy Laplace's equation.

$$\Delta_{(3)}\{aQ_{10}^3 + bQ_{01}^2Q_{10} + cQ_{11}^2Q_{10}\} = 6aQ_{01} + 2bQ_{10} + 2cQ_{10} = 0$$

$$\text{i.e. } 3a + b + c = 0$$

Two solutions are

$$b = -c \quad a = 0$$

$$b = c \quad a = -2/3 b$$

and the harmonic polynomials are

$$Q_{10}(Q_{01}^2 - Q_{11}^2) \text{ and}$$

$$2Q_{10}^3 - 3Q_{10}(Q_{01}^2 + Q_{11}^2).$$

The other components of the triply degenerate set are found by exactly the same linear combinations. It is noted that the treatment as presented here does not lead to the explicit form of the totally symmetric part of the total vibrational wave function. This can be deduced by a simple extension of the analysis of the isotropic oscillator. It in general consists of a Gaussian term times an inhomogeneous polynomial in the radial coordinate and was mentioned in section 4.4.3.

Taking the analysis one step further, $n = 4$ contains $\lambda = 0$ (A) and $\lambda = 2$ (E^+ , E^- , T) which must be subtracted from the total $n = 4$ basis ($2A + 2E^+ + 2E^- + 3T$).

The harmonic combination of the two A functions satisfies

$$\Delta_{(3)}\{(Q_{10}^4 + Q_{01}^4 + Q_{11}^4) + a(Q_{01}^2 Q_{11}^2 + Q_{11}^2 Q_{10}^2 + Q_{10}^2 Q_{01}^2)\} = 0$$

giving

$$12(Q_{10}^2 + Q_{01}^2 + Q_{11}^2) + 4a(Q_{10}^2 + Q_{01}^2 + Q_{11}^2) = 0$$

$$a = -3$$

and the harmonic polynomial is

$$(Q_{10}^4 + Q_{01}^4 + Q_{11}^4) - 3(Q_{01}^2 Q_{11}^2 + Q_{11}^2 Q_{10}^2 + Q_{10}^2 Q_{01}^2)$$

Similarly for two E^+ functions

$$\Delta_{(3)}\{Q_{10}^4 + \omega Q_{01}^4 + \omega^* Q_{11}^4 + a(Q_{01}^2 Q_{11}^2 + \omega Q_{11}^2 Q_{10}^2 + \omega^* Q_{10}^2 Q_{01}^2)\} = 0$$

giving

$$12Q_{10}^2 + 12\omega Q_{01}^2 + 12\omega^* Q_{11}^2 + 2a(\omega^* + \omega)Q_{01}^2 + 2a(1 + \omega^*)Q_{01}^2 + 2a(1 + \omega^*)Q_{11}^2 \\ = (12 - 2a)Q_{10}^2 + (12 - 2a)\omega^* Q_{01}^2 + (12 - 2a)\omega Q_{11}^2 = 0$$

i.e. $a = 6$

Similarly for E^- with ω and ω^* interchanged

$$(Q_{10}^4 + \omega Q_{01}^4 + \omega^* Q_{11}^4) + 6(Q_{01}^2 Q_{11}^2 + \omega Q_{11}^2 Q_{10}^2 + \omega^* Q_{10}^2 Q_{01}^2)$$

The determination of the two harmonic polynomial sets of type T follows similar lines to that for $n = 3$.

It is finally briefly noted that $n = 5$ contains $\lambda = 1$ (T) and 3 (A + 2T).

Subtracting, the $n = 5$ A homogeneous polynomial is not harmonic, the E^+ and E^- polynomials are harmonic and the six sets of T polynomials can be combined to give 3 sets of harmonic polynomials.

The resulting sets of harmonic polynomials up to $n = 5$ symmetry adapted to the group A_4 (T) are collected in the following table.

Table 4.6.4

λ	Harmonic polynomial	
$\lambda = 0$	1	A
$\lambda = 1$	$Q_{10}; Q_{01}; Q_{11}$	T
$\lambda = 2$	$Q_{10}^2 + \omega Q_{01}^2 + \omega^* Q_{11}^2$	E^+
	$Q_{10}^2 + \omega^* Q_{01}^2 + \omega Q_{11}^2$	E^-
	$Q_{01}Q_{11}; Q_{11}Q_{10}; Q_{10}Q_{01}$	T
$\lambda = 3$	$Q_{10}Q_{01}Q_{11}$	A
	$Q_{10}(Q_{01}^2 - Q_{11}^2); Q_{01}(Q_{11}^2 - Q_{10}^2); Q_{11}(Q_{10}^2 - Q_{01}^2)$	T
	$2Q_{10}^3 - 3Q_{10}(Q_{01}^2 + Q_{11}^2); 2Q_{01}^3 - 3Q_{01}(Q_{11}^2 + Q_{10}^2);$ $2Q_{11}^3 - 3Q_{11}(Q_{10}^2 + Q_{01}^2)$	T
$\lambda = 4$	$(Q_{10}^4 + Q_{01}^4 + Q_{11}^4) - 3(Q_{01}^2Q_{11}^2 + Q_{11}^2Q_{10}^2 + Q_{10}^2Q_{01}^2)$	A
	$(Q_{10}^4 + \omega Q_{01}^4 + \omega^* Q_{11}^4) + 6(Q_{01}^2Q_{11}^2 + \omega Q_{11}^2Q_{10}^2 + \omega^* Q_{10}^2Q_{01}^2)$	E^+
	$(Q_{10}^4 + \omega^* Q_{01}^4 + \omega Q_{11}^4) + 6(Q_{01}^2Q_{11}^2 + \omega^* Q_{11}^2Q_{10}^2 + \omega Q_{10}^2Q_{01}^2)$	E^-
	$Q_{01}Q_{11}(Q_{01}^2 - Q_{11}^2); Q_{11}Q_{10}(Q_{11}^2 - Q_{10}^2); Q_{10}Q_{01}(Q_{10}^2 - Q_{01}^2)$	T
	$Q_{01}Q_{11}(Q_{01}^2 + Q_{11}^2 - 6Q_{10}^2); Q_{11}Q_{10}(Q_{11}^2 + Q_{10}^2 - 6Q_{01}^2);$ $Q_{10}Q_{01}(Q_{10}^2 + Q_{01}^2 - 6Q_{11}^2)$	T

4.6.3 Analysis of four-fold degenerate vibrations.

As a final example an analysis is carried through for a group which does not correspond to one of the familiar three dimensional point groups. The lowest order such group is chosen: $W_{5,4}$. Properties of the group were described in section 2.7.3 and a description of the corresponding four dimensional point group given in section 3.5.

The defining relations of the group of order twenty are

$$A^5 = E \quad B^2 = E \quad AB = BA^4$$

$$C^2 = B \quad AC = CA^2 \quad BC = CB$$

and the character table is

		E	4A	5B	5C	5BC
Γ_{000}	(A)	1	1	1	1	1
Γ_{002}	(B)	1	1	1	-1	-1
Γ_{011}	(E ⁺)	1	1	-1	<i>i</i>	- <i>i</i>
Γ_{01-1}	(E ⁻)	1	1	-1	- <i>i</i>	<i>i</i>
$\Gamma_{1,2,-1,-2}$	(G)	4	-1	0	0	0

The Schönflies notation has again been introduced to give a familiar appearance to the symmetry symbols.

A table can also be constructed giving the effect of the symmetry operators on typical basis functions. Not all the group elements are written explicitly. For the block of

operators A^2 , A^2B , A^2C , A^2BC the pattern of A , AB , AC , ABC is repeated for the functions Ψ_1 , Ψ_{-1} , ... but the multipliers are squared:

$$\epsilon^1 \rightarrow \epsilon^2 \quad \epsilon^2 \rightarrow \epsilon^{-1} \quad \text{etc.}$$

The pattern is repeated for higher powers of A .

	Ψ_{000}	Ψ_{002}	Ψ_{011}	Ψ_{01-1}	Ψ_1	Ψ_{-1}	Ψ_2	Ψ_{-2}
E	Ψ_{000}	Ψ_{002}	Ψ_{011}	Ψ_{01-1}	Ψ_1	Ψ_{-1}	Ψ_2	Ψ_{-2}
B	Ψ_{000}	Ψ_{002}	$-\Psi_{011}$	$-\Psi_{01-1}$	Ψ_{-1}	Ψ_1	Ψ_{-2}	Ψ_2
C	Ψ_{000}	$-\Psi_{002}$	$i\Psi_{011}$	$-i\Psi_{01-1}$	Ψ_2	Ψ_{-2}	Ψ_{-1}	Ψ_1
BC	Ψ_{000}	$-\Psi_{002}$	$-i\Psi_{011}$	$i\Psi_{01-1}$	Ψ_{-2}	Ψ_2	Ψ_1	Ψ_{-1}
A	Ψ_{000}	Ψ_{002}	Ψ_{011}	Ψ_{01-1}	$\epsilon^1\Psi_1$	$\epsilon^{-1}\Psi_{-1}$	$\epsilon^2\Psi_2$	$\epsilon^{-2}\Psi_{-2}$
AB	Ψ_{000}	Ψ_{002}	$-\Psi_{011}$	$-\Psi_{01-1}$	$\epsilon^{-1}\Psi_{-1}$	$\epsilon^1\Psi_1$	$\epsilon^{-2}\Psi_{-2}$	$\epsilon^2\Psi_2$
AC	Ψ_{000}	$-\Psi_{002}$	$i\Psi_{011}$	$-i\Psi_{01-1}$	$\epsilon^2\Psi_2$	$\epsilon^{-2}\Psi_{-2}$	$\epsilon^{-1}\Psi_{-1}$	$\epsilon^1\Psi_1$
ABC	Ψ_{000}	$-\Psi_{002}$	$-i\Psi_{011}$	$i\Psi_{01-1}$	$\epsilon^{-2}\Psi_{-2}$	$\epsilon^2\Psi_2$	$\epsilon^1\Psi_1$	$\epsilon^{-1}\Psi_{-1}$

Here the overtone analysis of a four-fold degenerate (G) vibration will be carried through.

The basis functions Ψ_1 , Ψ_{-1} , Ψ_2 , Ψ_{-2} are complex conjugate pairs so that the analysis is closer to that for D_3 than T.

Unlike D_3 the harmonic polynomials cannot all be written straight down and linear combinations of the symmetry adapted homogeneous polynomials in the corresponding vibrational coordinates Q_1 Q_{-1} Q_2 Q_{-2} will be sought which are solutions of Laplace's equation in the form

$$\left(\sum_j \frac{\partial^2}{\partial Q_j \partial Q_j^*} \right) h_\lambda = 0$$

The analysis is simplified to some extent because the results found for a two dimensional oscillator can be used for complex conjugate pair such as $Q_1 Q_{-1}$ when this occurs separately. The analysis is now carried through in a similar way to the previous examples.

As always, the formal $n = 0$ polynomial 1 is both homogeneous and harmonic and corresponds to the ground state of the isotropic oscillator.

Similarly for $n = 1$, the set

$$Q_1; Q_{-1}; Q_2; Q_{-2}$$

has symmetry G and is both homogeneous and harmonic.

For $n = 2$ the symmetry adapted homogeneous polynomials are given in the following table

Homogeneous polynomial f_n	Symmetry
$Q_{-2}^2 \quad Q_2^2 \quad Q_1^2 \quad Q_{-1}^2$	G
$Q_1 Q_{-1} + Q_2 Q_{-2}$	A
$Q_1 Q_{-1} - Q_2 Q_{-2}$	B
$Q_{-1} Q_2 \quad Q_1 Q_{-2} \quad Q_{-1} Q_{-2} \quad Q_1 Q_2$	G

The set contains a member with A symmetry which corresponds to $\lambda = 0$ (i.e. zero angular momentum) and this coordinate is not harmonic. The remaining coordinates spanning

$B + 2G$

are homogeneous and harmonic.

In the case of $n = 3$, the symmetry adapted homogeneous polynomials are

Homogeneous polynomial f_n	Symmetry	$\Delta_{(4)}f_n$
$Q_2^3 \quad Q_{-2}^3 \quad Q_{-1}^3 \quad Q_1^3$	G	$= 0$
$Q_1^2 Q_{-1} \quad Q_1 Q_{-1}^2 \quad Q_2^2 Q_{-2} \quad Q_2 Q_{-2}^2$	G	$\neq 0$
$Q_{-1}^2 Q_{-2} \quad Q_1^2 Q_2 \quad Q_{-2}^2 Q_1 \quad Q_2^2 Q_{-1}$	G	$= 0$
$Q_1 Q_2^2 + Q_{-1} Q_{-2}^2 + Q_{-1}^2 Q_2 + Q_1^2 Q_{-2}$	A	$= 0$
$Q_1 Q_2^2 + Q_{-1} Q_{-2}^2 - Q_{-1}^2 Q_2 - Q_1^2 Q_{-2}$	B	$= 0$
$Q_1 Q_2^2 - Q_{-1} Q_{-2}^2 + i Q_{-1}^2 Q_2 - i Q_1^2 Q_{-2}$	E^+	$= 0$
$Q_1 Q_2^2 - Q_{-1} Q_{-2}^2 - i Q_{-1}^2 Q_2 + i Q_1^2 Q_{-2}$	E^-	$= 0$
$Q_1 Q_2 Q_{-2} \quad Q_{-1} Q_2 Q_{-2} \quad Q_1 Q_{-1} Q_2 \quad Q_1 Q_{-1} Q_{-2}$	G	$\neq 0$

An indication is given in each case as whether a polynomial as written is or is not already harmonic. This can be decided directly using the analysis from the doubly degenerate representation in D_3 , where the harmonic polynomials are either powers of Q_1 only or powers of Q_{-1} only. Therefore in the four dimensional case, a polynomial is not harmonic if it contains both Q_1 and Q_{-1} and or Q_2 and Q_{-2} . Otherwise it is harmonic. In this case, most

of the functions are already harmonic, and the remaining two sets of G functions must be combined to form one harmonic set.

Explicitly, using the first member of the degenerate set in each case

$$\Delta\{Q_1^2 Q_{-1} + a Q_1 Q_2 Q_{-2}\}$$

$$\propto \left(\frac{\partial^2}{\partial Q_1 \partial Q_{-1}} + \frac{\partial^2}{\partial Q_2 \partial Q_{-2}} \right) \{Q_1^2 Q_{-1} + a Q_1 Q_2 Q_{-2}\}$$

$$= (2 + a) Q_1$$

$$= 0 \text{ if } a = -2$$

Hence the harmonic polynomial is

$$Q_1^2 Q_{-1} - 2 Q_1 Q_2 Q_{-2}$$

with corresponding expressions for the other members. The whole set of harmonic polynomials is summarised in table 4.6.1.

The case of $n = 4$ follows a similar course. The full set of homogeneous polynomials which spans

$$3A + 2B + E^+ + E^- + 7G$$

is summarised in the following table:

Homogeneous polynomial f_n	Symmetry	Δf_n
$Q_{-1}^4 \quad Q_1^4 \quad Q_{-2}^4 \quad Q_2^4$	G	= 0
$Q_2 Q_{-2}^3 \quad Q_2^3 Q_{-2} \quad Q_1^3 Q_{-1} \quad Q_1 Q_{-1}^3$	G	$\neq 0$
$Q_1^3 Q_{-2} \quad Q_{-1}^3 Q_2 \quad Q_1 Q_2^3 \quad Q_{-1} Q_{-2}^3$	G	= 0
$Q_1^3 Q_2 + Q_{-1}^3 Q_{-2} + Q_{-1} Q_2^3 + Q_1 Q_{-2}^3$	A	= 0

$Q_1^3 Q_2 + Q_{-1}^3 Q_{-2} - Q_{-1} Q_2^3 - Q_1 Q_{-2}^3$	B	= 0
$Q_1^3 Q_2 - Q_{-1}^3 Q_{-2} + i Q_{-1} Q_2^3 - i Q_1 Q_{-2}^3$	E^+	= 0
$Q_1^3 Q_2 - Q_{-1}^3 Q_{-2} - i Q_{-1} Q_2^3 + i Q_1 Q_{-2}^3$	E^-	= 0
$Q_1^2 Q_{-1}^2 + Q_{-2}^2 Q_2^2$	A	$\neq 0$
$Q_1^2 Q_{-1}^2 - Q_{-2}^2 Q_2^2$	B	$\neq 0$
$Q_1^2 Q_2^2 - Q_{-1}^2 Q_{-2}^2 - Q_{-1}^2 Q_2^2 - Q_1^2 Q_{-2}^2$	G	= 0
$Q_1 Q_{-1} Q_{-2}^2 - Q_1 Q_{-1} Q_2^2 - Q_1^2 Q_2 Q_{-2} - Q_{-1}^2 Q_2 Q_{-2}$	G	$\neq 0$
$Q_{-1} Q_2^2 Q_{-2} - Q_1 Q_2 Q_{-2}^2 - Q_1 Q_{-1}^2 Q_{-2} - Q_1^2 Q_{-1} Q_2$	G	$\neq 0$
$Q_1 Q_{-1}^2 Q_2 - Q_1^2 Q_{-1} Q_{-2} - Q_{-1} Q_2 Q_{-2}^2 - Q_1 Q_2^2 Q_{-2}$	G	$\neq 0$
$Q_1 Q_{-1} Q_2 Q_{-2}$	A	$\neq 0$

As always, $n = 4$ includes angular momentum components $\lambda = 4, 2, 0$ and the harmonic polynomials correspond to $\lambda = 4$. From the earlier analysis $\lambda = 2$ goes with $B + 2G$ and $\lambda = 0$ with A. In this way the harmonic polynomials $n = 4, \lambda = 4$ span $2A + B + E^+ + E^- + 5G$.

Of the three A homogeneous polynomials, one is already harmonic and the other is found by combining the other two. The B, E^+ and E^- functions are given directly.

Of the seven G homogeneous functions, three are already harmonic and the other four must be combined to give the two missing harmonic functions. To achieve this the effect of the Laplacian on each homogeneous function is written down explicitly.

$$1/2\Delta(Q_2 Q_{-2}^3) = 3Q_{-2}^2$$

$$1/2\Delta(Q_1 Q_{-1} Q_{-2}^2) = Q_{-2}^2$$

$$1/2\Delta(Q_{-1}Q_2^2Q_{-2}) = 2Q_{-1}Q_2$$

$$1/2\Delta(Q_1Q_{-1}^2Q_2) = 2Q_{-1}Q_2.$$

From this it can be seen that a harmonic function can be formed from the first pair and the other from the second pair:

$$(Q_2Q_{-2}^3 - 3Q_1Q_{-1}Q_{-2}^2)$$

and

$$(Q_{-1}Q_2^2Q_{-2} - Q_1Q_{-1}^2Q_2)$$

the whole set of harmonic functions is given in table 4.6.1.

Finally the case of $n = 5$ is considered. The complete set of symmetry adapted homogeneous polynomials is given in the following table:

Homogeneous polynomials f_n	Symmetry	$\Delta_{(4)}f_n$
$Q_1^5 + Q_{-1}^5 + Q_2^5 + Q_{-2}^5$	A	= 0
$Q_1^5 + Q_{-1}^5 - Q_2^5 - Q_{-2}^5$	B	= 0
$Q_1^5 - Q_{-1}^5 + iQ_2^5 - iQ_{-2}^5$	E^+	= 0
$Q_1^5 - Q_{-1}^5 - iQ_2^5 + iQ_{-2}^5$	E^-	= 0
$Q_2^4Q_{-2} \quad Q_2Q_{-2}^4 \quad Q_1Q_{-1}^4 \quad Q_1^4Q_{-1}$	G	$4Q_2^3$
$Q_1^4Q_2 \quad Q_{-1}^4Q_{-2} \quad Q_{-1}Q_2^4 \quad Q_1Q_{-2}^4$	G	= 0
$Q_{-1}Q_{-2}^4 \quad Q_1Q_2^4 \quad Q_1^4Q_{-2} \quad Q_{-1}^4Q_2$	G	= 0
$Q_1^3Q_{-1}^2 \quad Q_1^2Q_{-1}^3 \quad Q_2^3Q_{-2}^2 \quad Q_2^2Q_{-2}^3$	G	$6Q_1^2Q_{-1}$
$Q_1^2Q_{-2}^3 \quad Q_{-1}^2Q_2^3 \quad Q_1^3Q_2^2 \quad Q_{-1}^3Q_{-2}^2$	G	= 0
$Q_{-1}^3Q_2^2 \quad Q_1^3Q_{-2}^2 \quad Q_{-1}^2Q_{-2}^3 \quad Q_1^2Q_2^3$	G	= 0

$Q_1 Q_{-1} Q_2^3 \quad Q_1 Q_{-1} Q_{-2}^3 \quad Q_{-1}^3 Q_2 Q_{-2} \quad Q_1^3 Q_2 Q_{-2}$	G	Q_2^3
$Q_1 Q_{-1}^3 Q_{-2} \quad Q_1^3 Q_{-1} Q_2 \quad Q_1 Q_2 Q_{-2}^3 \quad Q_{-1} Q_2^3 Q_{-2}$	G	$3Q_{-1}^2 Q_{-2}$
$Q_1^3 Q_{-1} Q_{-2} + Q_1 Q_{-1}^3 Q_2 + Q_1 Q_2^3 Q_{-2} + Q_{-1} Q_2 Q_{-2}^3$	A	$3Q_1^2 Q_{-2} + 3Q_{-1}^2 Q_2 +$ $3Q_1 Q_2^2 + 3Q_{-1} Q_{-2}^2$
$Q_1^3 Q_{-1} Q_{-2} + Q_1 Q_{-1}^3 Q_2 - Q_1 Q_2^3 Q_{-2} - Q_{-1} Q_2 Q_{-2}^3$	B	$3Q_1^2 Q_{-2} + 3Q_1 Q_2^2 -$ $3Q_{-1}^2 Q_2 - 3Q_{-1} Q_{-2}^2$
$Q_1^3 Q_{-1} Q_{-2} - Q_1 Q_{-1}^3 Q_2 + iQ_1 Q_2^3 Q_{-2} - iQ_{-1} Q_2 Q_{-2}^3$	E^+	$3Q_1^2 Q_{-2} - 3Q_1 Q_2^2 +$ $i3Q_{-1}^2 Q_2 - i3Q_{-1} Q_{-2}^2$
$Q_1^3 Q_{-1} Q_{-2} - Q_1 Q_{-1}^3 Q_2 - iQ_1 Q_2^3 Q_{-2} + iQ_{-1} Q_2 Q_{-2}^3$	E^-	$3Q_1^2 Q_{-2} - 3Q_1 Q_2^2 -$ $i3Q_{-1}^2 Q_2 + i3Q_{-1} Q_{-2}^2$
$Q_1^2 Q_2 Q_{-2}^2 + Q_{-1}^2 Q_2^2 Q_{-2} + Q_1^2 Q_{-1} Q_2^2 + Q_1 Q_{-1}^2 Q_{-2}^2$	A	$2Q_1^2 Q_{-2} + 2Q_{-1}^2 Q_2 +$ $2Q_1 Q_2^2 + 2Q_{-1} Q_{-2}^2$
$Q_1^2 Q_2 Q_{-2}^2 + Q_{-1}^2 Q_2^2 Q_{-2} - Q_1^2 Q_{-1} Q_2^2 + Q_1 Q_{-1}^2 Q_{-2}^2$	B	$2Q_1^2 Q_{-2} + 2Q_{-1}^2 Q_2 -$ $2Q_1 Q_2^2 - 2Q_{-1} Q_{-2}^2$
$Q_1^2 Q_2 Q_{-2}^2 - Q_{-1}^2 Q_2^2 Q_{-2} + iQ_1^2 Q_{-1} Q_2^2 - iQ_1 Q_{-1}^2 Q_{-2}^2$	E^+	$2Q_1^2 Q_{-2} - 2Q_{-1}^2 Q_2 +$ $i2Q_1 Q_2^2 - i2Q_{-1} Q_{-2}^2$
$Q_1^2 Q_2 Q_{-2}^2 - Q_{-1}^2 Q_2^2 Q_{-2} - iQ_1^2 Q_{-1} Q_2^2 + iQ_1 Q_{-1}^2 Q_{-2}^2$	E^-	$2Q_1^2 Q_{-2} - 2Q_{-1}^2 Q_2 -$ $i2Q_1 Q_2^2 + i2Q_{-1} Q_{-2}^2$
$Q_1 Q_2^2 Q_{-2}^2 \quad Q_{-1} Q_2^2 Q_{-2}^2 \quad Q_1^2 Q_{-1}^2 Q_{-2} \quad Q_1^2 Q_{-1}^2 Q_{-2}$	G	$4Q_1 Q_2 Q_{-2}$
$Q_{-1}^2 Q_2 Q_{-2}^2 \quad Q_1^2 Q_2^2 Q_{-2} \quad Q_1^2 Q_{-1} Q_{-2}^2 \quad Q_1 Q_{-1}^2 Q_2^2$	G	$2Q_{-1}^2 Q_{-2}$
$Q_1^2 Q_{-1} Q_2 Q_{-2} \quad Q_{-1}^2 Q_2 Q_{-2} Q_1 \quad Q_2^2 Q_{-2} Q_1 Q_{-1}$ $Q_{-2}^2 Q_1 Q_{-1} Q_2$	G	$(2Q_1 Q_2 Q_{-2} + Q_1^2 Q_{-1})$

Here the effect of the operator $1/2\Delta$ on the first function in each set is given explicitly to facilitate the ultimate construction of harmonic polynomials.

It is seen that pure functions Q_1^5 etc. may now be combined to form bases for non-degenerate representations. This emphasises that the procedure being followed has an underlying 5-fold character and that the various results follow 5-fold cycles.

The homogeneous functions span

$$3(A + B + E^+ + E^-) + 11G$$

and by appropriate subtraction the harmonic functions span

$$2(A + B + E^+ + E^-) + 7G$$

For the non-degenerate functions, one set is already harmonic and the other can be formed by combination of the remaining two. It can be seen that each is a combination of the same four functions, which therefore must be separately combined to satisfy Laplace's equation.

In the case of the G harmonic functions, three of them must be formed by combining 7 homogeneous functions. Consideration of the effects of the Laplacian operator readily enable them to be constructed.

The whole set is summarised in table 4.6.5.

Table 4.6.5

λ	Harmonic polynomial h_λ	Symmetry
0	1	A
1	$Q_1 \quad Q_{-1} \quad Q_2 \quad Q_{-2}$	G
2	$Q_{-2}^2 \quad Q_2^2 \quad Q_1^2 \quad Q_{-1}^2$	G
	$Q_1 Q_{-1} - Q_2 Q_{-2}$	B
	$Q_{-1} Q_2 \quad Q_1 Q_{-2} \quad Q_{-1} Q_{-2} \quad Q_1 Q_2$	G
n = 3	$Q_2^3 \quad Q_{-2}^3 \quad Q_{-1}^3 \quad Q_1^3$	G
	$Q_{-1}^2 Q_{-2} \quad Q_1^2 Q_2 \quad Q_{-2}^2 Q_1 \quad Q_2^2 Q_{-1}$	G
	$(Q_1^2 Q_{-1} - 2Q_1 Q_2 Q_{-2}) \quad (Q_1 Q_{-1}^2 - 2Q_{-1} Q_2 Q_{-2}) \quad (Q_2^2 Q_{-2} - 2Q_1 Q_{-1} Q_2)$ $(Q_2 Q_{-2}^2 - 2Q_1 Q_{-1} Q_{-2})$	G
	$Q_1 Q_2^2 + Q_{-1} Q_{-2}^2 + Q_{-1}^2 Q_2 + Q_1^2 Q_{-2}$	A
	$Q_1 Q_2^2 + Q_{-1} Q_{-2}^2 - Q_{-1}^2 Q_2 - Q_1^2 Q_{-2}$	B
	$Q_1 Q_2^2 - Q_{-1} Q_{-2}^2 + iQ_{-1}^2 Q_2 - iQ_1^2 Q_{-2}$	E^+
	$Q_1 Q_2^2 - Q_{-1} Q_{-2}^2 - iQ_{-1}^2 Q_2 + iQ_1^2 Q_{-2}$	E^-
n = 4	$Q_1^3 Q_2 + Q_{-1}^3 Q_{-2} + Q_{-1} Q_2^3 + Q_1 Q_{-2}^3$	A
	$(Q_1^2 Q_{-1}^2 + Q_{-2}^2 Q_2^2) - 4(Q_1 Q_{-1} Q_2 Q_{-2})$	A
	$Q_1^3 Q_2 + Q_{-1}^3 Q_{-2} - Q_{-1} Q_2^3 - Q_1 Q_{-2}^3$	B
	$Q_1^3 Q_2 - Q_{-1}^3 Q_{-2} + iQ_{-1} Q_2^3 - iQ_1 Q_{-2}^3$	E^+
	$Q_1^3 Q_2 - Q_{-1}^3 Q_{-2} - iQ_{-1} Q_2^3 + iQ_1 Q_{-2}^3$	E^-
	$Q_{-1}^4 \quad Q_1^4 \quad Q_{-2}^4 \quad Q_2^4$	G
	$Q_1^3 Q_{-2} \quad Q_{-1}^3 Q_2 \quad Q_1 Q_2^3 \quad Q_{-1} Q_{-2}^3$	G

	$Q_1^2 Q_2^2 \quad Q_{-1}^2 Q_{-2}^2 \quad Q_{-1}^2 Q_2^2 \quad Q_1^2 Q_{-2}^2$	G
	$(Q_2 Q_{-2}^3 - 3 Q_1 Q_{-1} Q_{-2}^2) \quad (Q_2^2 Q_{-2} - 3 Q_1 Q_{-1} Q_2^2) \quad (Q_1^3 Q_{-1} - 3 Q_1^2 Q_2 Q_{-2})$ $(Q_1 Q_{-1}^3 - 3 Q_{-1}^2 Q_2 Q_{-2})$	G
	$(Q_{-1} Q_2^2 Q_{-2} - Q_1 Q_{-1}^2 Q_2) \quad (Q_1 Q_2 Q_{-2}^2 - Q_1^2 Q_{-1} Q_{-2})$ $(Q_1 Q_{-1}^2 Q_{-2} - Q_{-1} Q_2 Q_{-2}^2) \quad (Q_1^2 Q_{-1} Q_2 - Q_1 Q_2^2 Q_{-2})$	G
n = 5	$Q_1^5 + Q_{-1}^5 + Q_2^5 + Q_{-2}^5$	A
	$Q_1^5 + Q_{-1}^5 - Q_2^5 - Q_{-2}^5$	B
	$Q_1^5 - Q_{-1}^5 + i Q_2^5 - i Q_{-2}^5$	E ⁺
	$Q_1^5 - Q_{-1}^5 - i Q_2^5 + i Q_{-2}^5$	E ⁻
	$2(Q_1^3 Q_{-1} Q_{-2} + Q_1 Q_{-1}^3 Q_2 + Q_1 Q_2^3 Q_{-2} + Q_1 Q_2 Q_{-2}^3) -$ $3(Q_1^2 Q_2 Q_{-2}^2 + Q_{-1}^2 Q_2^2 Q_{-2} + Q_1^2 Q_{-1} Q_2^2 + Q_1 Q_{-1}^2 Q_{-2}^2)$	A
	$2(Q_1^3 Q_{-1} Q_{-2} + Q_1 Q_{-1}^3 Q_2 - Q_1 Q_2^3 Q_{-2} - Q_1 Q_2 Q_{-2}^3) -$ $3(Q_1^2 Q_2 Q_{-2}^2 + Q_{-1}^2 Q_2^2 Q_{-2} - Q_1^2 Q_{-1} Q_2^2 - Q_1 Q_{-1}^2 Q_{-2}^2)$	B
	$2(Q_1^3 Q_{-1} Q_{-2} - Q_1 Q_{-1}^3 Q_2 + i Q_1 Q_2^3 Q_{-2} - i Q_1 Q_2 Q_{-2}^3) -$ $3(Q_1^2 Q_2 Q_{-2}^2 - Q_{-1}^2 Q_2^2 Q_{-2} + i Q_1^2 Q_{-1} Q_2^2 - i Q_1 Q_{-1}^2 Q_{-2}^2)$	E ⁺
	$2(Q_1^3 Q_{-1} Q_{-2} - Q_1 Q_{-1}^3 Q_2 - i Q_1 Q_2^3 Q_{-2} + i Q_1 Q_2 Q_{-2}^3) -$ $3(Q_1^2 Q_2 Q_{-2}^2 - Q_{-1}^2 Q_2^2 Q_{-2} - i Q_1^2 Q_{-1} Q_2^2 + i Q_1 Q_{-1}^2 Q_{-2}^2)$	E ⁻
	$Q_1^4 Q_2 \quad Q_{-1}^4 Q_{-2} \quad Q_2^4 Q_{-1} \quad Q_{-2}^4 Q_1$	G
	$Q_{-2}^4 Q_{-1} \quad Q_2^4 Q_1 \quad Q_1^4 Q_{-2} \quad Q_{-1}^4 Q_2$	G
	$Q_{-2}^3 Q_1^2 \quad Q_2^3 Q_{-1}^2 \quad Q_1^3 Q_2^2 \quad Q_{-1}^3 Q_{-2}^2$	G
	$Q_{-1}^3 Q_2^2 \quad Q_1^3 Q_{-2}^2 \quad Q_{-2}^3 Q_{-1}^2 \quad Q_2^3 Q_1^2$	G

	$(Q_2^4 Q_2 - 4Q_2^3 Q_1 Q_{-1}) \quad (Q_{-2}^4 Q_2 - 4Q_{-2}^3 Q_1 Q_{-1})$ $(Q_{-1}^4 Q_1 - 4Q_{-1}^3 Q_2 Q_{-2}) \quad (Q_1^4 Q_{-1} - 4Q_1^3 Q_2 Q_{-2})$	G
	$(2Q_1 Q_{-1}^3 Q_{-2} - 3Q_{-1}^2 Q_{-2}^2 Q_2) \quad (2Q_1^3 Q_{-1} Q_2 - 3Q_1^2 Q_2^2 Q_{-2})$ $(2Q_{-2}^3 Q_2 Q_1 - 3Q_1^2 Q_{-1}^2 Q_2) \quad (2Q_2^3 Q_{-1} Q_{-2} - 3Q_{-1}^2 Q_2^2 Q_1)$	G
	$(Q_1^3 Q_{-1}^2 + 3Q_2^2 Q_{-2}^2 Q_1 - 6Q_1^2 Q_{-1} Q_2 Q_{-2})$ $(Q_{-1}^3 Q_1^2 + 3Q_2^2 Q_{-2}^2 Q_{-1} - 6Q_{-1}^2 Q_2 Q_{-2} Q_1)$ $(Q_2^3 Q_{-2}^2 + 3Q_1^2 Q_{-2}^2 Q_{-1} - 6Q_2^2 Q_{-2} Q_1 Q_{-1})$ $(Q_{-2}^3 Q_2^2 + 3Q_1^2 Q_{-1}^2 Q_{-2} - 6Q_{-2}^2 Q_1 Q_{-1} Q_2)$	G

4.7 Concluding remarks.

In this chapter the symmetry properties of vibrational overtones have been discussed providing an example of an application of the methods developed in this thesis to a quantum mechanical problem contrasting with the geometrical considerations in the point group treatment.

The problem is multilayered because the natural classification of vibrational states in terms of a point group or space group is complicated by the use of the harmonic approximation. The problem is soluble at the harmonic level but in the case of degenerate oscillators there is a very high underlying symmetry resulting in extensive degeneracies. Reinclusion of the anharmonic terms restores the geometric symmetry of the nuclear framework and the problem is to adapt the harmonic functions to this lower symmetry.

The Hamiltonian of the degenerate harmonic (isotropic) oscillator characteristically contains the square of an angular momentum. The degeneracy of the oscillator is not restricted by the three dimensions of ordinary space and the angular momentum concerned is a generalisation of the concept of an arbitrarily high number of dimensions. It is found that the symmetry dependent parts of the eigenfunctions of the isotropic oscillator depend only on the angular momentum.

The symmetry problem under consideration here, can then be reduced to the adaptation of the functions belonging to a particular eigenvalue of the total angular momentum to the point or space group symmetry. This is exactly analogous to the problem encountered in ligand field theory where the atomic orbitals of a central metal

atom with angular momentum quantum number l (usually the d electrons) are adapted to, for example, the octahedral arrangement of ligands.

The present work is much more extensive covering both an arbitrary number of dimensions and an arbitrary number of the total angular quantum number. Such symmetry adapted angular momentum functions in the context of ligand field theory are known as lattice harmonics [41].

In dealing with three dimensional problems prominence is often given to formulations in which angular polar coordinates are used. Solution of the general case is facilitated by converting the angular functions once determined back to Cartesian coordinates.

Two of the examples treated in this chapter correspond to three dimensional point groups and involved two and three fold degeneracies only. It was thus not necessary to use the analysis of the special methods developed here. The example of a four fold degenerate vibration was somewhat artificial since it is not clear how such a system might actually be found physically. The most likely source of vibration problems involving degeneracies of four and higher is the crystalline state where such degeneracies are common.

APPENDICES.

A4.1 Solution Of The Isotropic Oscillator Using Operator Methods.

A4.1.1 The One Dimensional Harmonic Oscillator.

The Hamiltonian operator for a one dimensional harmonic oscillator has the simplified form

$$H = \frac{1}{2} \left(Q^2 - \frac{\partial^2}{\partial Q^2} \right) \quad (\text{A4.1.1})$$

The solution is conveniently expressed in terms of the operators [40]

$$\begin{aligned} a &= \frac{1}{\sqrt{2}} \left(Q + \frac{\partial}{\partial Q} \right) \\ a^+ &= \frac{1}{\sqrt{2}} \left(Q - \frac{\partial}{\partial Q} \right) \end{aligned} \quad (\text{A4.1.2})$$

which satisfy the commutation relation

$$[a, a^+] = 1$$

Then, the Hamiltonian operator becomes

$$H = 1/2(aa^+ + a^+a) \quad (\text{A4.1.3})$$

The eigenvalues are

$$E_n = (n + 1/2)$$

where the quantum number n can take the values 0, 1, 2, ...

The commutation relations of H with the operators are found to be

$$[H, a] = -a$$

$$[H, a^+] = a^+$$

These relations can be used to determine the effect of the operators a and a^+ on an eigenfunction of H . If Ψ_n and E_n are known solutions then,

$$Ha\Psi_n = (aH - a)\Psi_n = E_na\Psi_n - a\Psi_n = (E_n - 1)a\Psi_n$$

which shows that $a\Psi_n$ is an eigenfunction of H with eigenvalue given by $(E_n - 1)$. This

implies that

$$a\Psi_n \propto \Psi_{n-1}$$

Similarly

$$a^+\Psi_n \propto \Psi_{n+1}$$

The operators a and a^+ thus have the effect of reducing or increasing the quantum number n by one. The relationships

$$\begin{aligned} a\Psi_n &= (n)^{\frac{1}{2}}\Psi_{n-1} \\ a^-\Psi_n &= (n+1)^{\frac{1}{2}}\Psi_{n+1} \end{aligned} \tag{A4.1.4}$$

can be shown to conserve normalisation and the functions themselves satisfy the orthonormality relation

$$\int \Psi_m \Psi_n d\tau = \delta_{mn} \tag{A4.1.5}$$

Combination of (4) and (5) enable the matrix elements of a and a^+ to be evaluated so that for example

$$\begin{aligned} \int \Psi_m a\Psi_n d\tau &= n^{\frac{1}{2}}\delta_{m,n-1} \\ \int \Psi_m a^+\Psi_n d\tau &= (n+1)^{\frac{1}{2}}\delta_{m,n+1} \end{aligned}$$

By the usual rules of matrix multiplication the matrix elements of any product of powers of a and a^+ may be found.

Equations (2) can be inverted so that matrix elements of coordinates and momenta and their powers can be determined.

The explicit forms of the wave functions is necessary if their symmetry properties are to be considered. Physical considerations make it clear that there is a lowest eigenvalue so that the effect of the annihilation operator acting on the lowest eigenfunction is to give zero.

$$a\Psi_0 = 0$$

In the coordinate form we have

$$\frac{1}{\sqrt{2}} \left(Q + \frac{\partial}{\partial Q} \right) \Psi_0 = 0$$

for which the general solution is

$$\Psi_0 = A \exp(-Q^2/2)$$

where A is the normalisation constant. In the present context, normalised functions are not required and A can be set equal to unity. Unnormalised higher functions are generated by successive application of the creation operator a^+ . The resulting functions are given in the following table.

Table A4.1.1

n	Unnormalised function Ψ_n
0	$\exp(-Q^2/2)$
1	$2Q\exp(-Q^2/2)$
2	$(4Q^2-2)\exp(-Q^2/2)$
3	$(8Q^3-12Q)\exp(-Q^2/2)$
4	$(16Q^4-48Q^2+12)\exp(-Q^2/2)$

The non exponential factors are the Hermite polynomials which are connected by the recurrence relation

$$H_{n+1} = 2QH_n - 2nH_{n-1}.$$

A4.1.2 The Two Dimensional Isotropic Oscillator.

Real Coordinate Basis.

For the two dimensional isotropic oscillator, the Hamiltonian can be written as the sum of two one-dimensional terms, one for each coordinate.

$$H = \frac{1}{2} \sum_{j=1}^2 \left(Q_j^2 - \frac{\partial^2}{\partial Q_j^2} \right) \quad (\text{A4.2.1})$$

The Hamiltonian is separable in the two coordinates and the problem may be completely solved using the appropriate combinations of the one-dimensional solutions.

Annihilation and creation operators are defined for each coordinate as in (A4.1.2) with the commutator

$$[a_j, a_k^+] = \delta_{jk} \quad (\text{A4.2.2})$$

and Hamiltonian

$$H = \frac{1}{2} \sum_{j=1}^2 (a_j a_j^+ + a_j^+ a_j) \quad (\text{A4.2.3})$$

Now, the eigenfunctions depend on two quantum numbers with

$$H \Psi_{n_j n_k} = (n_j + n_k + 1) \Psi_{n_j n_k} \quad (\text{A4.2.4})$$

and they satisfy the orthonormality relation

$$\int \Psi_{m_1 m_2} \Psi_{n_1 n_2} d\tau = \delta_{m_1 n_1, m_2 n_2}$$

The eigenvalues are now degenerate as the energy depends on the sum of the two quantum numbers

$$n = n_j + n_k \quad (\text{A4.2.5})$$

The energy level labeled by the quantum number n is $(n+1)$ -fold degenerate. The corresponding wave functions are constructed by taking products of the one-dimensional functions given in table A4.1.1, one factor for each coordinate Q_i with its identifying quantum number n_i . The first few examples are given in the following table.

Table A4.2.1

n :	n_1	n_2	Unnormalised function Ψ_n
0	0	0	$\exp[-1/2(Q_1^2+Q_2^2)]$
1	1	0	$2Q_1\exp[-1/2(Q_1^2+Q_2^2)]$
	0	1	$2Q_2\exp[-1/2(Q_1^2+Q_2^2)]$
2	2	0	$(4Q_1^2-2)\exp[-1/2(Q_1^2+Q_2^2)]$
	0	2	$(4Q_2^2-2)\exp[-1/2(Q_1^2+Q_2^2)]$
	1	1	$4Q_1Q_2\exp[-1/2(Q_1^2+Q_2^2)]$
3	3	0	$(8Q_1^3-12Q_1)\exp[-1/2(Q_1^2+Q_2^2)]$
	0	3	$(8Q_2^3-12Q_2)\exp[-1/2(Q_1^2+Q_2^2)]$
	2	1	$(8Q_1^2Q_2-4Q_2)\exp[-1/2(Q_1^2+Q_2^2)]$
	1	2	$(8Q_1Q_2^2-4Q_1)\exp[-1/2(Q_1^2+Q_2^2)]$

This treatment can be applied to an isotropic oscillator of arbitrarily high dimension. The two dimensional case may also be solved in terms of a pair of complex conjugate coordinates.

Complex Coordinates Bases.

In terms of a pair of complex conjugate coordinates Q_+ and Q_- defined as

$$\begin{aligned} Q_+ &= \frac{1}{\sqrt{2}}(Q_1 + iQ_2) \\ Q_- &= \frac{1}{\sqrt{2}}(Q_1 - iQ_2) \end{aligned} \quad (\text{A4.2.6})$$

the Hamiltonian operator for the two dimensional isotropic oscillator becomes

$$H = \left(Q_+ Q_- - \frac{\partial^2}{\partial Q_+ \partial Q_-} \right) \quad (\text{A4.2.7})$$

Annihilation and creation operators may be defined as

$$\begin{aligned} b_- &= \frac{1}{\sqrt{2}} \left(Q_+ + \frac{\partial}{\partial Q_-} \right) \\ b_+ &= \frac{1}{\sqrt{2}} \left(Q_- + \frac{\partial}{\partial Q_+} \right) \\ b_-^+ &= \frac{1}{\sqrt{2}} \left(Q_- - \frac{\partial}{\partial Q_+} \right) \\ b_+^+ &= \frac{1}{\sqrt{2}} \left(Q_+ - \frac{\partial}{\partial Q_-} \right) \end{aligned} \quad (\text{A4.2.8})$$

and these satisfy the commutation relations

$$[b_j, b_k^+] = \delta_{jk}$$

$$[b_j, b_k] = 0 \quad j, k = +, -$$

$$[b_j^+, b_k^+] = 0$$

The Hamiltonian then becomes

$$H = \frac{1}{2} (b_+ b_+^+ + b_+^+ b_+ + b_- b_-^+ + b_-^+ b_-) \quad (\text{A4.2.9})$$

Comparison with (A4.2.3) shows that these two forms of the Hamiltonian are essentially the same and this suggests that the effect of the new operators has an equivalent form;

$$\begin{aligned} b_+ \Psi_{n_+, n_-} &= n_+^{\frac{1}{2}} \Psi_{n_+-1, n_-} \\ b_+^+ \Psi_{n_+, n_-} &= (n_+ + 1)^{\frac{1}{2}} \Psi_{n_++1, n_-} \end{aligned} \quad (\text{A4.2.10})$$

with similar expressions for b_- and b_-^+ acting on the functions and changing the quantum number n_- .

Also the form of the wave equation is equivalent to (A4.2.4)

$$H \Psi_{n_+, n_-} = (n_+ + n_- + 1) \Psi_{n_+, n_-} \quad (\text{A4.2.11})$$

However, the wave functions associated with the complex coordinates are not equivalent to the real coordinate forms. In terms of the complex coordinates the (unnormalised) ground state function has the form

$$\Psi_{00} = \exp(-Q_+ Q_-)$$

Again, higher functions are formed by successive application of the creation operators b_+^+ and b_-^+ . These are summarised in the following table.

Table A4.2.2

n:	n_+	n_-	Unnormalised function
0	0	0	$\exp(-Q \cdot Q_+)$
1	1	0	$2Q_+ \exp(-Q \cdot Q_+)$
	0	1	$2Q_- \exp(-Q \cdot Q_+)$
2	2	0	$4Q_+^2 \exp(-Q \cdot Q_+)$
	0	2	$4Q_-^2 \exp(-Q \cdot Q_+)$
	1	1	$(4Q_+Q_- - 2) \exp(-Q \cdot Q_+)$
3	3	0	$8Q_+^3 \exp(-Q \cdot Q_+)$
	0	3	$8Q_-^3 \exp(-Q \cdot Q_+)$
	2	1	$8Q_+(Q_+Q_- - 1) \exp(-Q \cdot Q_+)$
	1	2	$8Q_-(Q_+Q_- - 1) \exp(-Q \cdot Q_+)$

A4.2 Angular Momentum In two Dimensions.

The two-dimensional isotropic oscillator is a special case because it has only one component of angular momentum

$$M_{(2)}^2 = M_{12}^2$$

and it is therefore possible to write down an operator for the angular momentum (M_{12}) itself. This may be written in various forms related to the descriptions introduced in appendix A4.1.2.

$$M = -i \left(Q_1 \frac{\partial}{\partial Q_2} - Q_2 \frac{\partial}{\partial Q_1} \right)$$

$$M = -i(a_1^+ a_2 - a_1 a_2^+)$$

$$M = Q_- \frac{\partial}{\partial Q_-} - Q_+ \frac{\partial}{\partial Q_+}$$

$$M = \frac{1}{2}(b_+ b_+^+ + b_+^+ b_+ - b_- b_-^+ - b_-^+ b_-)$$

These forms of the angular momentum operator are all quadratic as indeed is the Hamiltonian (A4.2.3 and A4.2.9). Matrix elements in the two forms are readily evaluated and the non zero elements are as follows

$$\int \Psi_{n_1+1, n_2-1} M \Psi_{n_1 n_2} d\tau = -i n_2^{\frac{1}{2}} (n_1 + 1)^{\frac{1}{2}}$$

$$\int \Psi_{n_1-1, n_2+1} M \Psi_{n_1 n_2} d\tau = i (n_2 + 1)^{\frac{1}{2}} n_1^{\frac{1}{2}}$$

$$\int \Psi_{n_1 n_2} M \Psi_{n_1 n_2} d\tau = (n_+ - n_-)$$

In the complex description

$$H\Psi_{n_+, n_-} = (n_+ + n_- + 1)\Psi_{n_+, n_-}$$

and

$$M\Psi_{n_+, n_-} = (n_+ - n_-)\Psi_{n_+, n_-}$$

In this way the energy is characterised by a single quantum number $n = n_+ + n_-$ and the angular momentum by $m = n_+ - n_-$. The degeneracy pattern can then be summarised

$n = 0$	$m = 0$
$n = 1$	$m = +1, -1$
$n = 2$	$m = +2, 0, -2$
$n = 3$	$m = +3, +1, -1, -3$
n	$m = +n, n-2, \dots, -n$

The positive and negative values correspond to opposite sense of rotation.

Closer investigation of the two-dimensional isotropic oscillator functions in complex form shows that they are closely related to polar coordinates and may be separated into factors.

a) Q_+^n equivalent to $r^n \exp(in\phi)$

Q_-^n equivalent to $r^n \exp(-in\phi)$

b) A polynomial in $Q_+ Q_- = r^2$ which is identical with an associated Laguerre polynomial thus connecting with the most usual text book treatment.

CHAPTER FIVE: CONCLUDING REMARKS.

In this thesis some aspects of the application of symmetry theory to problems in molecular quantum mechanics have been considered. A feature has been that the properties of groups have been derived from first principles. The result has been that the properties come only from a purely abstract definition of the group and do not depend on any preconceptions about the physical nature of any associated problem. A limitation is that the method only applies to solvable groups but since this includes most three dimensional point groups and all three dimensional space groups most possible systems are included.

Emphasis has been placed on problems in which the ruling dimensionality is greater than three and it has been shown that many dimensional point groups can be constructed from abstract definitions using the solvable group method. The geometrical significance of symmetry operations in the general d -dimensional case has been deduced from the properties of orthogonal and unitary matrices and a number of four dimensional point groups in particular have been described in detail. It would be interesting to extend the treatment to generate a complete list of such groups. A further interesting question would be can the approach being employed here be applied to generate space groups as well as point groups?

The analysis of the vibrational overtone problem involved the harmonic oscillator, the many dimensional angular momentum and the geometrical symmetry group and so provided an interesting example of the three main constituents of theoretical chemistry. It has been seen that this can readily be applied to molecular problems and there is no

reason in principle why crystal vibrations should not be analysed in the same way. This could well form the subject of future work.

It has been emphasised that the methods used in this thesis are appropriate to solvable groups. The commonly occurring groups which are not solvable relate to the regular icosahedron and a number of interesting physical problems are associated with this symmetry. The consideration of such groups would form the results of a complete thesis in itself.

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