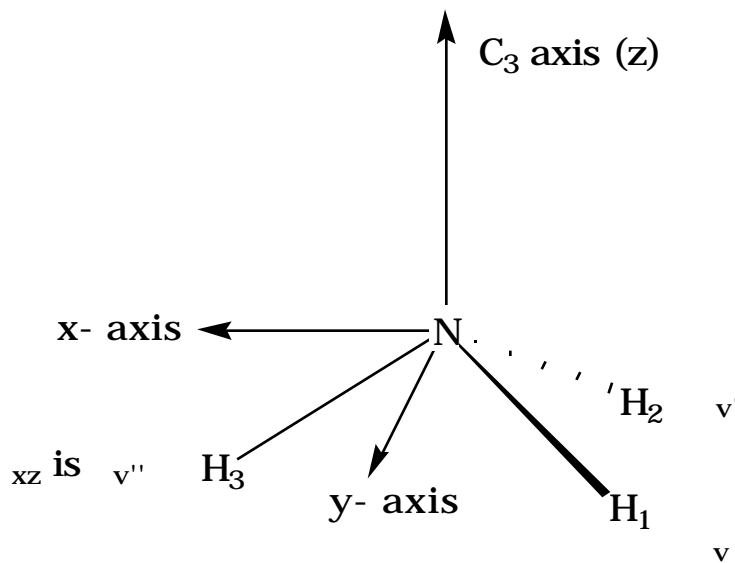


Point Group Symmetry E

It is assumed that the reader has previously learned, in undergraduate inorganic or physical chemistry classes, how symmetry arises in molecular shapes and structures and what symmetry elements are (e.g., planes, axes of rotation, centers of inversion, etc.). For the reader who feels, after reading this appendix, that additional background is needed, the texts by Cotton and EWK, as well as most physical chemistry texts can be consulted. We review and teach here only that material that is of direct application to symmetry analysis of molecular orbitals and vibrations and rotations of molecules. We use a specific example, the ammonia molecule, to introduce and illustrate the important aspects of point group symmetry.

I. The C_{3v} Symmetry Group of Ammonia - An Example

The ammonia molecule NH_3 belongs, in its ground-state equilibrium geometry, to the C_{3v} point group. Its symmetry operations consist of two C_3 rotations, C_3 , C_3^2 (rotations by 120° and 240° , respectively about an axis passing through the nitrogen atom and lying perpendicular to the plane formed by the three hydrogen atoms), three vertical reflections, σ_v , σ_v' , σ_v'' , and the identity operation. Corresponding to these six operations are symmetry elements: the three-fold rotation axis, C_3 and the three symmetry planes σ_v , σ_v' and σ_v'' that contain the three NH bonds and the z-axis (see figure below).



These six symmetry operations form a mathematical group. A group is defined as a set of objects satisfying four properties.

1. A combination rule is defined through which two group elements are combined to give a result which we call the product. The product of two elements in the group must also be a member of the group (i.e., the group is closed under the combination rule).
2. One special member of the group, when combined with any other member of the group, must leave the group member unchanged (i.e., the group contains an identity element).

- Every group member must have a reciprocal in the group. When any group member is combined with its reciprocal, the product is the identity element.
- The associative law must hold when combining three group members (i.e., $(AB)C$ must equal $A(BC)$).

The members of symmetry groups are symmetry operations; the combination rule is successive operation. The identity element is the operation of doing nothing at all. The group properties can be demonstrated by forming a multiplication table. Let us label the rows of the table by the first operation and the columns by the second operation. Note that this order is important because most groups are not commutative. The C_{3v} group multiplication table is as follows:

	E	C_3	C_3^2	ν	ν'	ν''	second operation
E	E	C_3	C_3^2	ν	ν'	ν''	
C_3	C_3	C_3^2	E	ν'	ν''	ν	
C_3^2	C_3^2	E	C_3	ν''	ν	ν'	
ν	ν	ν''	ν'	E	C_3^2	C_3	
ν'	ν'	ν	ν''	C_3	E	C_3^2	
ν''	ν''	ν'	ν	C_3^2	C_3	E	
First operation							

Note the reflection plane labels do not move. That is, although we start with H_1 in the ν plane, H_2 in ν'' , and H_3 in ν' , if H_1 moves due to the first symmetry operation, ν remains fixed and a different H atom lies in the ν plane.

II. Matrices as Group Representations

In using symmetry to help simplify molecular orbital or vibration/rotation energy level calculations, the following strategy is followed:

- A set of M objects belonging to the constituent atoms (or molecular fragments, in a more general case) is introduced. These objects are the orbitals of the individual atoms (or of the fragments) in the m.o. case; they are unit vectors along the x , y , and z directions located on each of the atoms, and representing displacements along each of these directions, in the vibration/rotation case.
- Symmetry tools are used to combine these M objects into M new objects each of which belongs to a specific symmetry of the point group. Because the hamiltonian (electronic in the m.o. case and vibration/rotation in the latter case) commutes with the symmetry operations of the point group, the matrix representation of \mathbf{H} within the symmetry adapted basis will be "block diagonal". That is, objects of different symmetry will not interact; only interactions among those of the same symmetry need be considered.

To illustrate such symmetry adaptation, consider symmetry adapting the $2s$ orbital of N and the three $1s$ orbitals of H. We begin by determining how these orbitals transform under the symmetry operations of the C_{3v} point group. The act of each of the six symmetry operations on the four atomic orbitals can be denoted as follows:

(S_N, S_1, S_2, S_3)	E	(S_N, S_1, S_2, S_3)
	C_3	(S_N, S_3, S_1, S_2)
	C_3^2	(S_N, S_2, S_3, S_1)
	ν	(S_N, S_1, S_3, S_2)
	ν''	(S_N, S_3, S_2, S_1)
	ν'	(S_N, S_2, S_1, S_3)

Here we are using the active view that a C_3 rotation rotates the molecule by 120° . The equivalent passive view is that the 1s basis functions are rotated -120° . In the C_3 rotation, S_3 ends up where S_1 began, S_1 , ends up where S_2 began and S_2 ends up where S_3 began.

These transformations can be thought of in terms of a matrix multiplying a vector with elements (S_N, S_1, S_2, S_3) . For example, if $D^{(4)}(C_3)$ is the representation matrix giving the C_3 transformation, then the above action of C_3 on the four basis orbitals can be expressed as:

$$D^{(4)}(C_3) \begin{pmatrix} S_N \\ S_1 \\ S_2 \\ S_3 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} S_N \\ S_1 \\ S_2 \\ S_3 \end{pmatrix} = \begin{pmatrix} S_N \\ S_3 \\ S_1 \\ S_2 \end{pmatrix}$$

We can likewise write matrix representations for each of the symmetry operations of the C_{3v} point group:

$$D^{(4)}(C_3^2) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \quad D^{(4)}(E) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

$$D^{(4)}(\nu) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \quad D^{(4)}(\nu') = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

$$D^{(4)}(\sigma_v'') = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

It is easy to verify that a C_3 rotation followed by a σ_v reflection is equivalent to a σ_v' reflection alone. In other words

$$\sigma_v C_3 = \sigma_v', \text{ or, } \begin{matrix} & S_1 & & S_3 & & S_3 \\ & & C_3 & & & \\ \sigma_v C_3 = \sigma_v' & S_2 & S_3 & S_1 & S_2 & S_2 & S_1 \end{matrix}$$

Note that this same relationship is carried by the matrices:

$$D^{(4)}(\sigma_v) D^{(4)}(C_3) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} = D^{(4)}(\sigma_v')$$

Likewise we can verify that $C_3 \sigma_v = \sigma_v''$ directly and we can notice that the matrices also show the same identity:

$$D^{(4)}(C_3) D^{(4)}(\sigma_v) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = D^{(4)}(\sigma_v'')$$

In fact, one finds that the six matrices, $D^{(4)}(R)$, when multiplied together in all 36 possible ways obey the same multiplication table as did the six symmetry operations. We say the matrices form a representation of the group because the matrices have all the properties of the group.

A. Characters of Representations

One important property of a matrix is the sum of its diagonal elements

$$\text{Tr}(D) = \sum_i D_{ii} = \chi$$

is called the trace or character of the matrix. In the above example

$$\chi(E) = 4$$

$$\chi(C_3) = \chi(C_3^2) = 1$$

$$\chi(\sigma_v) = \chi(\sigma_v') = \chi(\sigma_v'') = 2.$$

The importance of the characters of the symmetry operations lies in the fact that they do not depend on the specific basis used to form them. That is, they are invariant to a unitary or orthogonal transformation of the objects used to define the matrices. As a result, they contain information about the symmetry operation itself and about the space spanned by the set of objects. The significance of this observation for our symmetry adaptation process will become clear later.

Note that the characters of both rotations are the same as are those of all three reflections. Collections of operations having identical characters are called classes. Each operation in a class of operations has the same character as other members of the class. The character of a class depends on the space spanned by the basis of functions on which the symmetry operations act. Above we used (S_N, S_1, S_2, S_3) as a basis.

B. Another Basis and Another Representation

If, alternatively, we use the one-dimensional basis consisting of the 1s orbital on the N-atom, we obtain different characters, as we now demonstrate.

The act of the six symmetry operations on this S_N can be represented as follows:

$$\begin{array}{ccc} S_N \begin{array}{c} E \\ S_N \end{array} S_N; & S_N \begin{array}{c} C_3 \\ S_N \end{array} S_N; & S_N \begin{array}{c} C_3^2 \\ S_N \end{array} S_N; \\ S_N \begin{array}{c} \nu \\ S_N \end{array} S_N; & S_N \begin{array}{c} \nu' \\ S_N \end{array} S_N; & S_N \begin{array}{c} \nu'' \\ S_N \end{array} S_N. \end{array}$$

We can represent this group of operations in this basis by the one-dimensional set of matrices:

$$\begin{array}{ccc} D^{(1)}(E) = 1; & D^{(1)}(C_3) = 1; & D^{(1)}(C_3^2) = 1, \\ D^{(1)}(\nu) = 1; & D^{(1)}(\nu'') = 1; & D^{(1)}(\nu') = 1. \end{array}$$

Again we have

$$D^{(1)}(\nu) D^{(1)}(C_3) = 1 \quad 1 = D^{(1)}(\nu''), \text{ and}$$

$$D^{(1)}(C_3) D^{(1)}(\nu) = 1 \quad 1 = D^{(1)}(\nu').$$

These six matrices form another representation of the group. In this basis, each character is equal to unity. The representation formed by allowing the six symmetry operations to act on the 1s N-atom orbital is clearly not the same as that formed when the same six operations acted on the (S_N, S_1, S_2, S_3) basis. We now need to learn how to further analyze the information content of a specific representation of the group formed when the symmetry operations act on any specific set of objects.

III. Reducible and Irreducible Representations

A. A Reducible Representation

Note that every matrix in the four dimensional group representation labeled $D^{(4)}$ has the so-called block diagonal form

$$\begin{array}{|c|ccc|} \hline 1 & 0 & 0 & 0 \\ \hline 0 & \multicolumn{3}{|c|}{3 \times 3 \text{ matrix}} \\ \hline 0 & & & \\ \hline 0 & & & \\ \hline \end{array}$$

This means that these $D^{(4)}$ matrices are really a combination of two separate group representations (mathematically, it is called a direct sum representation). We say that $D^{(4)}$ is reducible into a one-dimensional representation $D^{(1)}$ and a three-dimensional representation formed by the 3×3 submatrices which we will call $D^{(3)}$.

$$\begin{array}{l}
 \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{array} ; \quad \begin{array}{ccc} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{array} ; \quad \begin{array}{ccc} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{array} \\
 D^{(3)}(E) = & & \\
 \\
 \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{array} ; \quad \begin{array}{ccc} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{array} ; \quad \begin{array}{ccc} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{array} \\
 D^{(3)}(\nu) = & & \\
 \end{array}$$

The characters of $D^{(3)}$ are $\chi(E) = 3$, $\chi(2C_3) = 0$, $\chi(3\nu) = 1$. Note that we would have obtained this $D^{(3)}$ representation directly if we had originally chosen to examine the basis (S_1, S_2, S_3) ; also note that these characters are equal to those of $D^{(4)}$ minus those of $D^{(1)}$.

B. A Change in Basis

Now let us convert to a new basis that is a linear combination of the original S_1, S_2, S_3 basis:

$$T_1 = S_1 + S_2 + S_3$$

$$T_2 = 2S_1 - S_2 - S_3$$

$$T_3 = S_2 - S_3$$

(Don't worry about how we construct T_1 , T_2 , and T_3 yet. As will be demonstrated later, we form them by using symmetry projection operators defined below) We determine how the "T" basis functions behave under the group operations by allowing the operations to act on the S_j and interpreting the results in terms of the T_i . In particular,

$$\begin{array}{l}
 (T_1, T_2, T_3) \xrightarrow{\nu} (T_1, T_2, -T_3); \quad (T_1, T_2, T_3) \xrightarrow{E} (T_1, T_2, T_3); \\
 (T_1, T_2, T_3) \xrightarrow{\nu'} (S_3 + S_2 + S_1, 2S_3 - S_2 - S_1, S_2 - S_1) = (T_1, -\frac{1}{2}T_2 - \frac{3}{2}T_3, -\frac{1}{2}T_2 + \frac{1}{2}T_3); \\
 (T_1, T_2, T_3) \xrightarrow{\nu''} (S_2 + S_1 + S_3, 2S_2 - S_1 - S_3, S_1 - S_3) = (T_1, -\frac{1}{2}T_2 + \frac{3}{2}T_3, \frac{1}{2}T_2 + \frac{1}{2}T_3); \\
 (T_1, T_2, T_3) \xrightarrow{C_3} (S_3 + S_1 + S_2, 2S_3 - S_1 - S_2, S_1 - S_2) = (T_1, -\frac{1}{2}T_2 - \frac{3}{2}T_3, \frac{1}{2}T_2 - \frac{1}{2}T_3); \\
 (T_1, T_2, T_3) \xrightarrow{C_3^2} (S_2 + S_3 + S_1, 2S_2 - S_3 - S_1, S_3 - S_1) = (T_1, -\frac{1}{2}T_2 + \frac{3}{2}T_3, -\frac{1}{2}T_2 - \frac{1}{2}T_3).
 \end{array}$$

So the matrix representations in the new T_i basis are:

$$\begin{aligned}
D^{(3)}(E) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} ; D^{(3)}(C_3) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{3}{2} \\ 0 & +\frac{1}{2} & -\frac{1}{2} \end{pmatrix} ; \\
D^{(3)}(C_3^2) &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & +\frac{3}{2} \\ 0 & +\frac{1}{2} & -\frac{1}{2} \end{pmatrix} ; D^{(3)}(v) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} ; \\
D^{(3)}(v') &= \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{3}{2} \\ 0 & +\frac{1}{2} & -\frac{1}{2} \end{pmatrix} ; D^{(3)}(v'') = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & +\frac{3}{2} \\ 0 & +\frac{1}{2} & +\frac{1}{2} \end{pmatrix} .
\end{aligned}$$

C. Reduction of the Reducible Representation

These six matrices can be verified to multiply just as the symmetry operations do; thus they form another three-dimensional representation of the group. We see that in the T_i basis the matrices are block diagonal. This means that the space spanned by the T_i functions, which is the same space as the S_j span, forms a reducible representation that can be decomposed into a one dimensional space and a two dimensional space (via formation of the T_i functions). Note that the characters (traces) of the matrices are not changed by the change in bases.

The one-dimensional part of the above reducible three-dimensional representation is seen to be the same as the totally symmetric representation we arrived at before, $D^{(1)}$. The two-dimensional representation that is left can be shown to be irreducible; it has the following matrix representations:

$$\begin{aligned}
D^{(2)}(E) &= \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} ; D^{(2)}(C_3) = \begin{pmatrix} -\frac{1}{2} & -\frac{3}{2} \\ +\frac{1}{2} & -\frac{1}{2} \end{pmatrix} ; D^{(2)}(C_3^2) = \begin{pmatrix} -\frac{1}{2} & +\frac{3}{2} \\ -\frac{1}{2} & -\frac{1}{2} \end{pmatrix} ; \\
D^{(2)}(v) &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} ; D^{(2)}(v') = \begin{pmatrix} -\frac{1}{2} & -\frac{3}{2} \\ -\frac{1}{2} & +\frac{1}{2} \end{pmatrix} ; D^{(2)}(v'') = \begin{pmatrix} -\frac{1}{2} & +\frac{3}{2} \\ +\frac{1}{2} & +\frac{1}{2} \end{pmatrix} .
\end{aligned}$$

The characters can be obtained by summing diagonal elements:

$$(E) = 2, \quad (2C_3) = -1, \quad (3v) = 0.$$

D. Rotations as a Basis

Another one-dimensional representation of the group can be obtained by taking rotation about the Z-axis (the C_3 axis) as the object on which the symmetry operations act:

$$\begin{array}{lll} \text{E} & & \\ R_Z & R_Z; & R_Z^{C_3} R_Z; R_Z^{C_3^2} R_Z'; \\ R_Z^v & -R_Z; & R_Z^{v''} -R_Z; R_Z^{v'} -R_Z. \end{array}$$

In writing these relations, we use the fact that reflection reverses the sense of a rotation. The matrix representations corresponding to this one-dimensional basis are:

$$\begin{array}{lll} D^{(1)}(E) = 1; & D^{(1)}(C_3) = 1; & D^{(1)}(C_3^2) = 1; \\ D^{(1)}(v) = -1; & D^{(1)}(v'') = -1; & D^{(1)}(v') = -1. \end{array}$$

These one-dimensional matrices can be shown to multiply together just like the symmetry operations of the C_{3v} group. They form an irreducible representation of the group (because it is one-dimensional, it can not be further reduced). Note that this one-dimensional representation is not identical to that found above for the 1s N-atom orbital, or the T_1 function.

E. Overview

We have found three distinct irreducible representations for the C_{3v} symmetry group; two different one-dimensional and one two dimensional representations. Are there any more? An important theorem of group theory shows that the number of irreducible representations of a group is equal to the number of classes. Since there are three classes of operation, we have found all the irreducible representations of the C_{3v} point group. There are no more.

The irreducible representations have standard names the first $D^{(1)}$ (that arising from the T_1 and $1s_N$ orbitals) is called A_1 , the $D^{(1)}$ arising from R_z is called A_2 and $D^{(2)}$ is called E (not to be confused with the identity operation E).

Thus, our original $D^{(4)}$ representation was a combination of two A_1 representations and one E representation. We say that $D^{(4)}$ is a direct sum representation: $D^{(4)} = 2A_1 + E$. A consequence is that the characters of the combination representation $D^{(4)}$ can be obtained by adding the characters of its constituent irreducible representations.

		E	$2C_3$	$3\sigma_v$
A_1		1	1	1
A_1		1	1	1
E		2	-1	0
$2A_1 + E$		4	1	2

F. How to Decompose Reducible Representations in General

Suppose you were given only the characters (4,1,2). How can you find out how many times A_1 , E, and A_2 appear when you reduce $D^{(4)}$ to its irreducible parts? You want to find a linear combination of the characters of A_1 , A_2 and E that add up (4,1,2). You can treat the characters of matrices as vectors and take the dot product of A_1 with $D^{(4)}$

$$\begin{array}{cccccc}
 & & & & & 4 & E \\
 & & & & & 1 & C_3 \\
 1 & 1 & 1 & 1 & 1 & 1 & \\
 E & C_3 & & & & 2 & \nu \\
 & & & & & 2 & \\
 & & & & & 2 &
 \end{array} = 4 + 1 + 1 + 2 + 2 + 2 = 12.$$

The vector (1,1,1,1,1,1) is not normalized; hence to obtain the component of (4,1,1,2,2,2) along a unit vector in the (1,1,1,1,1,1) direction, one must divide by the norm of

(1,1,1,1,1,1); this norm is 6. The result is that the reducible representation contains $\frac{12}{6} = 2$

A_1 components. Analogous projections in the E and A_2 directions give components of 1 and 0, respectively. In general, to determine the number n of times irreducible

representation appears in the reducible representation with characters χ_{red} , one calculates

$$n = \frac{1}{g} \sum_R \chi(R) \chi_{red}(R),$$

where g is the order of the group and $\chi(R)$ are the characters of the i th irreducible representation.

G. Commonly Used Bases

We could take any set of functions as a basis for a group representation. Commonly used sets include: coordinates (x,y,z) located on the atoms of a polyatomic molecule (their symmetry treatment is equivalent to that involved in treating a set of p orbitals on the same atoms), quadratic functions such as d orbitals - xy,yz,xz,x²-y²,z², as well as rotations about the x, y and z axes. The transformation properties of these very commonly used bases are listed in the character tables shown at the end of this appendix.

H. Summary

The basic idea of symmetry analysis is that any basis of orbitals, displacements, rotations, etc. transforms either as one of the irreducible representations or as a direct sum (reducible) representation. Symmetry tools are used to first determine how the basis transforms under action of the symmetry operations. They are then used to decompose the resultant representations into their irreducible components.

III. Another Example

A. The 2p Orbitals of Nitrogen

For a function to transform according to a specific irreducible representation means that the function, when operated upon by a point-group symmetry operator, yields a linear combination of the functions that transform according to that irreducible representation. For example, a 2p_z orbital (z is the C₃ axis of NH₃) on the nitrogen atom belongs to the A₁ representation because it yields unity times itself when C₃, C₃², ν , ν' , ν'' or the identity operation act on it. The factor of 1 means that 2p_z has A₁ symmetry

since the characters (the numbers listed opposite A_1 and below E , $2C_3$, and $3\sigma_v$ in the C_{3v} character table) of all six symmetry operations are 1 for the A_1 irreducible representation.

The $2p_x$ and $2p_y$ orbitals on the nitrogen atom transform as the E representation since C_3 , C_3^2 , σ_v , σ_v' , σ_v'' and the identity operation map $2p_x$ and $2p_y$ among one another. Specifically,

$$\begin{array}{l} C_3 \\ C_3^2 \\ E \\ \sigma_v \\ \sigma_v' \\ \sigma_v'' \end{array} \begin{array}{l} 2p_x \\ 2p_y \\ 2p_x \\ 2p_y \\ 2p_x \\ 2p_y \\ 2p_x \\ 2p_y \\ 2p_x \\ 2p_y \\ 2p_x \\ 2p_y \\ 2p_x \\ 2p_y \end{array} = \begin{array}{l} \cos 120^\circ \quad -\sin 120^\circ \\ \sin 120^\circ \quad \cos 120^\circ \\ \cos 240^\circ \quad -\sin 240^\circ \\ \sin 240^\circ \quad \cos 240^\circ \\ 1 \quad 0 \\ 0 \quad 1 \\ -1 \quad 0 \\ 0 \quad 1 \\ +\frac{1}{2} \quad +\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} \quad -\frac{1}{2} \\ +\frac{1}{2} \quad -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} \quad -\frac{1}{2} \end{array} \begin{array}{l} 2p_x \\ 2p_y \\ 2p_x \\ 2p_y \\ 2p_x \\ 2p_y \\ 2p_x \\ 2p_y \\ 2p_x \\ 2p_y \\ 2p_x \\ 2p_y \\ 2p_x \\ 2p_y \end{array} ;$$

The 2 x 2 matrices, which indicate how each symmetry operation maps $2p_x$ and $2p_y$ into some combinations of $2p_x$ and $2p_y$, are the representation matrices ($D^{(IR)}$) for that particular operation and for this particular irreducible representation (IR). For example,

$$\begin{array}{l} +\frac{1}{2} \quad +\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} \quad -\frac{1}{2} \end{array} = D^{(E)}(\sigma_v')$$

This set of matrices have the same characters as $D^{(2)}$ above, but the individual matrix elements are different because we used a different basis set (here $2p_x$ and $2p_y$; above it was T_2 and T_3). This illustrates the invariance of the trace to the specific representation; the trace only depends on the space spanned, not on the specific manner in which it is spanned.

B. A Short-Cut

A short-cut device exists for evaluating the trace of such representation matrices (that is, for computing the characters). The diagonal elements of the representation matrices

are the projections along each orbital of the effect of the symmetry operation acting on that orbital. For example, a diagonal element of the C_3 matrix is the component of $C_3 2p_y$ along the $2p_y$ direction. More rigorously, it

is $\int 2p_y \cdot C_3 2p_y d\tau$. Thus, the character of the C_3 matrix is the sum of $\int 2p_x \cdot C_3 2p_x d\tau$ and $\int 2p_y \cdot C_3 2p_y d\tau$. In general, the character of any symmetry operation S can be computed by allowing S to operate on each orbital ψ_i , then projecting $S \psi_i$ along ψ_i (i.e., forming $\int \psi_i^* S \psi_i d\tau$), and summing these terms,

$$\chi(S) = \sum_i \int \psi_i^* S \psi_i d\tau = \text{Tr}(S).$$

If these rules are applied to the $2p_x$ and $2p_y$ orbitals of nitrogen within the C_{3v} point group, one obtains

$$\chi(E) = 2, \quad \chi(C_3) = \chi(C_3^2) = -1, \quad \chi(\sigma_v) = \chi(\sigma_v'') = \chi(\sigma_v') = 0.$$

This set of characters is the same as $D^{(2)}$ above and agrees with those of the E representation for the C_{3v} point group. Hence, $2p_x$ and $2p_y$ belong to or transform as the E representation. This is why (x,y) is to the right of the row of characters for the E representation in the C_{3v} character table. In similar fashion, the C_{3v} character table states that $d_{x^2-y^2}$ and d_{xy} orbitals on nitrogen transform as E , as do d_{xy} and d_{yz} , but d_z^2 transforms as A_1 .

Earlier, we considered in some detail how the three $1s_H$ orbitals on the hydrogen atoms transform. Repeating this analysis using the short-cut rule just described, the traces (characters) of the 3×3 representation matrices are computed by allowing E , $2C_3$, and $3\sigma_v$ to operate on $1s_{H1}$, $1s_{H2}$, and $1s_{H3}$ and then computing the component of the resulting function along the original function. The resulting characters are $\chi(E) = 3$, $\chi(C_3) = \chi(C_3^2) = 0$, and $\chi(\sigma_v) = \chi(\sigma_v') = \chi(\sigma_v'') = 1$, in agreement with what we calculated before.

Using the orthogonality of characters taken as vectors we can reduce the above set of characters to $A_1 + E$. Hence, we say that our orbital set of three $1s_H$ orbitals forms a reducible representation consisting of the sum of A_1 and E IR's. This means that the three $1s_H$ orbitals can be combined to yield one orbital of A_1 symmetry and a pair that transform according to the E representation.

IV. Projector Operators: Symmetry Adapted Linear Combinations of Atomic Orbitals

To generate the above A_1 and E symmetry-adapted orbitals, we make use of so-called symmetry projection operators P_E and P_{A_1} . These operators are given in terms of linear combinations of products of characters times elementary symmetry operations as follows:

$$P_{A_1} = \frac{1}{h} \sum_S \chi_A(S) S$$

$$P_E = \frac{1}{S} \sum_E \chi_E(S) S$$

where S ranges over $C_3, C_3^2, \sigma_v, \sigma_v'$ and σ_v'' and the identity operation. The result of applying P_{A_1} to say $1s_{H_1}$ is

$$\begin{aligned} P_{A_1} 1s_{H_1} &= 1s_{H_1} + 1s_{H_2} + 1s_{H_3} + 1s_{H_2} + 1s_{H_3} + 1s_{H_1} \\ &= 2(1s_{H_1} + 1s_{H_2} + 1s_{H_3}) = A_1, \end{aligned}$$

which is an (unnormalized) orbital having A_1 symmetry. Clearly, this same A_1 would be generated by P_{A_1} acting on $1s_{H_2}$ or $1s_{H_3}$. Hence, only one A_1 orbital exists.

Likewise,

$$P_E 1s_{H_1} = \frac{2}{3} (1s_{H_1} - 1s_{H_2} - 1s_{H_3}) = E_{1,1}$$

which is one of the symmetry adapted orbitals having E symmetry. The other E orbital can be obtained by allowing P_E to act on $1s_{H_2}$ or $1s_{H_3}$:

$$P_E 1s_{H_2} = \frac{2}{3} (1s_{H_2} - 1s_{H_1} - 1s_{H_3}) = E_{2,2}$$

$$P_E 1s_{H_3} = \frac{2}{3} (1s_{H_3} - 1s_{H_1} - 1s_{H_2}) = E_{3,3}$$

It might seem as though three orbitals having E symmetry were generated, but only two of these are really independent functions. For example, $E_{3,3}$ is related to $E_{1,1}$ and $E_{2,2}$ as follows:

$$E_{3,3} = -(E_{1,1} + E_{2,2})$$

Thus, only $E_{1,1}$ and $E_{2,2}$ are needed to span the two-dimensional space of the E representation. If we include $E_{1,1}$ in our set of orbitals and require our orbitals to be orthogonal, then we must find numbers a and b such that $\psi_E = a \psi_{E,2} + b \psi_{E,3}$ is

orthogonal to $E_{1,1}$: $\int \psi_E \psi_{E,1} d\tau = 0$. A straightforward calculation gives $a = -b$ or $\psi_E = a(1s_{H_2} - 1s_{H_3})$ which agrees with what we used earlier to construct the T_i functions in terms of the S_j functions.

V. Summary

Let us now summarize what we have learned. Any given set of atomic orbitals $\{\psi_i\}$, atom-centered displacements or rotations can be used as a basis for the symmetry operations of the point group of the molecule. The characters $\chi(S)$ belonging to the operations S of this point group within any such space can be found by summing the integrals $\int \psi_i^* S \psi_i d\tau$ over all the atomic orbitals (or corresponding unit vector atomic displacements). The resultant characters will, in general, be reducible to a combination of the characters of the irreducible representations $\chi_i(S)$. To decompose the characters $\chi(S)$ of the reducible representation to a sum of characters $\chi_i(S)$ of the irreducible representation

$$\chi(\mathbf{S}) = \sum_i n_i \chi_i(\mathbf{S}),$$

it is necessary to determine how many times, n_i , the i -th irreducible representation occurs in the reducible representation. The expression for n_i is (see the text by Cotton)

$$n_i = \frac{1}{g} \sum_{\mathbf{S}} \chi(\mathbf{S}) \chi_i(\mathbf{S})$$

in which g is the order of the point group; the total number of symmetry operations in the group (e.g., $g = 6$ for C_{3v}).

For example, the reducible representation $\chi(E) = 3$, $\chi(C_3) = 0$, and $\chi(\sigma_v) = 1$ formed by the three $1s_H$ orbitals discussed above can be decomposed as follows:

$$n_{A_1} = \frac{1}{6} (3 + 1 + 2 + 0 + 1 + 3 + 1 + 1) = 1,$$

$$n_{A_2} = \frac{1}{6} (3 + 1 + 2 + 0 + 1 + 3 + 1 + (-1)) = 0,$$

$$n_E = \frac{1}{6} (3 + 2 + 2 + 0 + (-1) + 3 + 1 + 0) = 1.$$

These equations state that the three $1s_H$ orbitals can be combined to give one A_1 orbital and, since E is degenerate, one pair of E orbitals, as established above. With knowledge of the n_i , the symmetry-adapted orbitals can be formed by allowing the projectors

$$P_i = \sum_{\mathbf{S}} \chi_i(\mathbf{S}) \mathbf{S}$$

to operate on each of the primitive atomic orbitals. How this is carried out was illustrated for the $1s_H$ orbitals in our earlier discussion. These tools allow a symmetry decomposition of any set of atomic orbitals into appropriate symmetry-adapted orbitals.

Before considering other concepts and group-theoretical machinery, it should once again be stressed that these same tools can be used in symmetry analysis of the translational, vibrational and rotational motions of a molecule. The twelve motions of NH_3 (three translations, three rotations, six vibrations) can be described in terms of combinations of displacements of each of the four atoms in each of three (x, y, z) directions. Hence, unit vectors placed on each atom directed in the x , y , and z directions form a basis for action by the operations $\{S\}$ of the point group. In the case of NH_3 , the characters of the resultant 12×12 representation matrices form a reducible representation in the C_{2v} point group: $\chi(E) = 12$, $\chi(C_3) = \chi(C_3^2) = 0$, $\chi(\sigma_v) = \chi(\sigma_v') = \chi(\sigma_v'') = 2$.

(You should try to prove this. For example under σ_v , the H_2 and H_3 atoms are interchanged, so unit vectors on either one will not contribute to the trace. Unit z -vectors on N and H_1 remain unchanged as well as the corresponding y -vectors. However, the x -vectors on N and H_1 are reversed in sign. The total character for σ_v' the H_2 and H_3 atoms are interchanged, so unit vectors on either one will not contribute to the trace. Unit z -vectors on N and H_1 remain unchanged as well as the corresponding y -vectors.

However, the x -vectors on N and H_1 are reversed in sign. The total character for σ_v'' is thus $4 - 2 = 2$. This representation can be decomposed as follows:

$$n_{A_1} = \frac{1}{6} [1 + 1 + 12 + 2 + 1 + 0 + 3 + 1 + 2] = 3,$$

$$n_{A_2} = \frac{1}{6} [1 + 1 + 12 + 2 + 1 + 0 + 3 + (-1) + 2] = 1,$$

$$n_E = \frac{1}{6} [1 + 2 + 12 + 2 + (-1) + 0 + 3 + 0 + 2] = 4.$$

From the information on the right side of the C_{3v} character table, translations of all four atoms in the z, x and y directions transform as $A_1(z)$ and $E(x,y)$, respectively, whereas rotations about the z(R_z), x(R_x), and y(R_y) axes transform as A_2 and E. Hence, of the twelve motions, three translations have A_1 and E symmetry and three rotations have A_2 and E symmetry. This leaves six vibrations, of which two have A_1 symmetry, none have A_2 symmetry, and two (pairs) have E symmetry. We could obtain symmetry-adapted vibrational and rotational bases by allowing symmetry projection operators of the irreducible representation symmetries to operate on various elementary cartesian (x,y,z) atomic displacement vectors. Both Cotton and Wilson, Decius and Cross show in detail how this is accomplished.

VI. Direct Product Representations

A. Direct Products in N-Electron Wavefunctions

We now return to the symmetry analysis of orbital products. Such knowledge is important because one is routinely faced with constructing symmetry-adapted N-electron configurations that consist of products of N individual orbitals. A point-group symmetry operator S, when acting on such a product of orbitals, gives the product of S acting on each of the individual orbitals

$$S(\psi_1 \psi_2 \psi_3 \dots \psi_N) = (S \psi_1) (S \psi_2) (S \psi_3) \dots (S \psi_N).$$

For example, reflection of an N-orbital product through the σ_v plane in NH_3 applies the reflection operation to all N electrons.

Just as the individual orbitals formed a basis for action of the point-group operators, the configurations (N-orbital products) form a basis for the action of these same point-group operators. Hence, the various electronic configurations can be treated as functions on which S operates, and the machinery illustrated earlier for decomposing orbital symmetry can then be used to carry out a symmetry analysis of configurations.

Another shortcut makes this task easier. Since the symmetry adapted individual orbitals $\{\psi_i, i = 1, \dots, M\}$ transform according to irreducible representations, the representation matrices for the N-term products shown above consist of products of the matrices belonging to each ψ_i . This matrix product is not a simple product but a direct product. To compute the characters of the direct product matrices, one multiplies the characters of the individual matrices of the irreducible representations of the N orbitals that appear in the electron configuration. The direct-product representation formed by the orbital products can therefore be symmetry-analyzed (reduced) using the same tools as we used earlier.

For example, if one is interested in knowing the symmetry of an orbital product of the form $a_1^2 a_2^2 e^2$ (note: lower case letters are used to denote the symmetry of electronic orbitals) in C_{3v} symmetry, the following procedure is used. For each of the six symmetry operations in the C_{2v} point group, the product of the characters associated with each of the six spin orbitals (orbital multiplied by \uparrow or \downarrow spin) is formed

$$\chi_i(S) = (\chi_{A_1}(S))^2 (\chi_{A_2}(S))^2 (\chi_E(S))^2.$$

In the specific case considered here, $\chi(E) = 4$, $\chi(2C_3) = 1$, and $\chi(3C_2) = 0$ (You should try this.). Notice that the contributions of any doubly occupied nondegenerate orbitals (e.g., a_1^2 , and a_2^2) to these direct product characters $\chi(S)$ are unity because for all operators $(\chi_k(S))^2 = 1$ for any one-dimensional irreducible representation. As a result, only the singly occupied or degenerate orbitals need to be considered when forming the characters of the reducible direct-product representation $\chi(S)$. For this example this means that the direct-product characters can be determined from the characters $\chi_E(S)$ of the two active (i.e., nonclosed-shell) orbitals - the e^2 orbitals. That is, $\chi(S) = \chi_E(S) \chi_E(S)$.

From the direct-product characters $\chi(S)$ belonging to a particular electronic configuration (e.g., $a_1^2 a_2^2 e^2$), one must still decompose this list of characters into a sum of irreducible characters. For the example at hand, the direct-product characters $\chi(S)$ decompose into one A_1 , one A_2 , and one E representation. This means that the e^2 configuration contains A_1 , A_2 , and E symmetry elements. Projection operators analogous to those introduced earlier for orbitals can be used to form symmetry-adapted orbital products from the individual basis orbital products of the form $a_1^2 a_2^2 e_x^m e_y^{m'}$, where m and m' denote the occupation (1 or 0) of the two degenerate orbitals e_x and e_y . When dealing with indistinguishable particles such as electrons, it is also necessary to further project the resulting orbital products to make them antisymmetric (for Fermions) or symmetric (for Bosons) with respect to interchange of any pair of particles. This step reduces the set of N -electron states that can arise. For example, in the above e^2 configuration case, only 3A_2 , 1A_1 , and 1E states arise; the 3E , 3A_1 , and 1A_2 possibilities disappear when the antisymmetry projector is applied. In contrast, for an $e^1 e^1$ configuration, all states arise even after the wavefunction has been made antisymmetric. The steps involved in combining the point group symmetry with permutational antisymmetry are illustrated in Chapter 10. In Appendix III of Electronic Spectra and Electronic Structure of Polyatomic Molecules, G. Herzberg, Van Nostrand Reinhold Co., New York, N.Y. (1966) the resolution of direct products among various representations within many point groups are tabulated.

B. Direct Products in Selection Rules

Two states ψ_a and ψ_b that are eigenfunctions of a Hamiltonian H_0 in the absence of some external perturbation (e.g., electromagnetic field or static electric field or potential due to surrounding ligands) can be "coupled" by the perturbation V only if the symmetries of V and of the two wavefunctions obey a so-called selection rule. In particular, only if the coupling integral (see Appendix D which deals with time independent perturbation theory)

$$\int \psi_a^* V \psi_b d\tau = V_{a,b}$$

is non-vanishing will the two states be coupled by V .

The role of symmetry in determining whether such integrals are non-zero can be demonstrated by noting that the integrand, considered as a whole, must contain a component that is invariant under all of the group operations (i.e., belongs to the totally

symmetric representation of the group). In terms of the projectors introduced above in Sec. IV, of this Appendix we must have

$$A(S) S_a^* V_b$$

not vanish. Here the subscript A denotes the totally symmetric representation of the group. The symmetry of the product $S_a^* V_b$ is, according to what was covered earlier in this Section, given by the direct product of the symmetries of S_a^* of V and of b . So, the conclusion is that the integral will vanish unless this triple direct product contains, when it is reduced to its irreducible components, a component of the totally symmetric representation.

To see how this result is used, consider the integral that arises in formulating the interaction of electromagnetic radiation with a molecule within the electric-dipole approximation:

$$S_a^* \mathbf{r}_b d .$$

Here \mathbf{r} is the vector giving, together with e , the unit charge, the quantum mechanical dipole moment operator

$$\mathbf{r} = e \sum_n Z_n \mathbf{R}_n - e \sum_j \mathbf{r}_j ,$$

where Z_n and \mathbf{R}_n are the charge and position of the n^{th} nucleus and \mathbf{r}_j is the position of the j^{th} electron. Now, consider evaluating this integral for the singlet $n \rightarrow n^*$ transition in formaldehyde. Here, the closed-shell ground state is of 1A_1 symmetry and the excited state, which involves promoting an electron from the non-bonding b_2 lone pair orbital on the Oxygen into the a_2 orbital on the CO moiety, is of 1A_2 symmetry ($b_1 \times b_2 = a_2$). The direct product of the two wavefunction symmetries thus contains only a_2 symmetry. The three components (x, y, and z) of the dipole operator have, respectively, b_1 , b_2 , and a_1 symmetry. Thus, the triple direct products give rise to the following possibilities:

$$a_2 \times b_1 = b_2,$$

$$a_2 \times b_2 = b_1,$$

$$a_2 \times a_1 = a_2 .$$

There is no component of a_1 symmetry in the triple direct product, so the integral vanishes. This allows us to conclude that the $n \rightarrow n^*$ excitation in formaldehyde is electric dipole forbidden.

VII. Overview

This appendix has reviewed how to make a symmetry decomposition of a basis of atomic orbitals (or cartesian displacements or orbital products) into irreducible representation components. This tool is most helpful when constructing the orbital correlation diagrams that form the basis of the Woodward-Hoffmann rules. We also learned how to form the direct-product symmetries that arise when considering configurations consisting of products of symmetry-adapted spin orbitals. This step is essential for the construction of configuration and state correlation diagrams upon which one ultimately bases a prediction about whether a reaction is allowed or forbidden. Finally, we learned how the direct product analysis allows one to determine whether or not integrals of products of wave functions with operators between them vanish. This tool is of utmost importance in determining selection rules in spectroscopy and for

determining the effects of external perturbations on the states of the species under investigation.

Character Tables

C_1	E
A	1

C_s	E	h		
A'	1	1	x, y, R_z	x^2, y^2, z^2, xy
A''	1	-1	z, R_x, R_y	yz, xz

C_i	E	i		
A_g	1	1	R_x, R_y, R_z	$x^2, y^2, z^2, xy, xz, yz$
A_u	1	-1	x, y, z	

C_2	E	C_2		
A	1	1	z, R_z	x^2, y^2, z^2, xy
B	1	-1	x, y, R_x, R_y	yz, xz

D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$		
A	1	1	1	1		x^2, y^2, z^2
B_1	1	1	-1	-1	z, R_z	xy
B_2	1	-1	1	-1	y, R_y	xz
B_3	1	-1	-1	1	x, R_x	yz

D_3	E	$2C_3$	$3C_2$		
A_1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	-1	z, R_z	
E	2	-1	0	$(x, y) (R_x, R_y)$	$(x^2 - y^2, xy) (xz, yz)$

D ₄	E	2C ₄	C ₂ (=C ₄ ²)	2C ₂ '	2C ₂ "		
A ₁	1	1	1	1	1	z, R _Z	x ² +y ² , z ²
A ₂	1	1	1	-1	-1		x ² -y ²
B ₁	1	-1	1	1	-1		xy
B ₂	1	-1	1	-1	1		(xz, yz)
E	2	0	-2	0	0		(x, y) (R _x , R _y)

C _{2v}	E	C ₂	v(xz)	v'(yz)		
A ₁	1	1	1	1	z	x ² , y ² , z ²
A ₂	1	1	-1	-1	R _Z	xy
B ₁	1	-1	1	-1	x, R _y	xz
B ₂	1	-1	-1	1	y, R _x	yz

C _{3v}	E	2C ₃	3 v		
A ₁	1	1	1	z	x ² +y ² , z ²
A ₂	1	1	-1	R _Z	
E	2	-1	0	(x, y) (R _x , R _y)	(x ² -y ² , xy) (xz, yz)

C _{4v}	E	2C ₄	C ₂	2 v	2 d		
A ₁	1	1	1	1	1	z	x ² +y ² , z ²
A ₂	1	1	1	-1	-1	R _Z	
B ₁	1	-1	1	1	-1		x ² -y ²
B ₂	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(x, y) (R _x , R _y)	(xz, yz)

C _{2h}	E	C ₂	i	h		
A _g	1	1	1	1	R _Z	x ² , y ² , z ² , xy
B _g	1	-1	1	-1	R _x , R _y	xz, yz
A _u	1	1	-1	-1	z	
B _u	1	-1	-1	1	x, y	

D _{2h}	E	C ₂ (z)	C ₂ (y)	C ₂ (x)	i	(xy)	(xz)	(yz)		
A _g	1	1	1	1	1	1	1	1		x ² ,y ² ,z ²
B _{1g}	1	1	-1	-1	1	1	-1	-1	R _z	xy
B _{2g}	1	-1	1	-1	1	-1	1	-1	R _y	xz
B _{3g}	1	-1	-1	1	1	-1	-1	1	R _x	yz
A _u	1	1	1	1	-1	-1	-1	-1		
B _{1u}	1	1	-1	-1	-1	-1	1	1	z	
B _{2u}	1	-1	1	-1	-1	1	-1	1	y	
B _{3u}	1	-1	-1	1	-1	1	1	-1	x	

D _{3h}	E	2C ₃	3C ₂	h	2S ₃	3 v		
A ₁ '	1	1	1	1	1	1		x ² +y ² ,z ²
A ₂ '	1	1	-1	1	1	-1	R _z	
E'	2	-1	0	2	-1	0	(x,y)	(x ² -y ² ,xy)
A ₁ "	1	1	1	-1	-1	-1		
A ₂ "	1	1	-1	-1	-1	1	z	
E"	2	-1	0	-2	1	0	(R _x ,R _y)	(xz,yz)

D _{4h}	E	2C ₄	C ₂	2C ₂ '	2C ₂ "	i	2S ₄	h	2 v	2 d		
A _{1g}	1	1	1	1	1	1	1	1	1	1		x ² +y ² ,z ²
A _{2g}	1	1	1	-1	-1	1	1	1	-1	-1	R _z	
B _{1g}	1	-1	1	1	-1	1	-1	1	1	-1		x ² -y ²
B _{2g}	1	-1	1	-1	1	1	-1	1	-1	1		xy
E _g	2	0	-2	0	0	2	0	-2	0	0	(R _x ,R _y)	(xz,yz)
A _{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A _{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z	
B _{1u}	1	-1	1	1	-1	-1	1	-1	-1	1		
B _{2u}	1	-1	1	-1	1	-1	1	-1	1	-1		
E _u	2	0	-2	0	0	-2	0	2	0	0	(x,y)	

D _{6h}	E	2C ₆	2C ₃	C ₂	3C ₂ '	3C ₂ "	i	2S ₃	2S ₆	h	3 d	3 v			
A _{1g}	1	1	1	1	1	1	1	1	1	1	1	1		R _Z	x ² +y ² ,z ²
A _{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1			
B _{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1			
B _{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1			
E _{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	(R _x ,R _y)	(xz,yz)	
E _{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		(x ² -y ² ,xy)	
A _{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1			
A _{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	z		
B _{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1			
B _{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1			
E _{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0	(x,y)		
E _{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0			

D _{2d}	E	2S ₄	C ₂	2C ₂ '	2 d			
A ₁	1	1	1	1	1		R _Z	x ² +y ² ,z ²
A ₂	1	1	1	-1	-1			
B ₁	1	-1	1	1	-1			x ² -y ²
B ₂	1	-1	1	-1	1	z		xy
E	2	0	-2	0	0	(x,y) (R _x ,R _y)		(xz,yz)

D _{3d}	E	2C ₃	3C ₂	i	2S ₆	3 d			
A _{1g}	1	1	1	1	1	1		R _Z	x ² +y ² ,z ²
A _{2g}	1	1	-1	1	1	-1			
E _g	2	-1	0	2	-1	0	(R _x ,R _y)	(x ² -y ² ,xy) (xz,yz)	
A _{1u}	1	1	1	-1	-1	-1			
A _{2u}	1	1	-1	-1	-1	1	z		
E _u	2	-1	0	-2	1	0	(x,y)		

S ₄	E	S ₄	C ₂	S ₄ ³			
A	1	1	1	1		R _Z	x ² +y ² ,z ²
B	1	-1	1	-1		z	x ² -y ² ,xy
E	{ 1 -1 }	{ i -i }	{ -1 -1 }	{ -i i }		(x,y) (R _x ,R _y)	(xz,yz)

T	E	4C ₃	4C ₃ ²	3C ₂		=exp(2 i/3)
A	1	1	1	1		x ² +y ² +z ²
E	{1 1	*	*	{1 -1}		(2z ² -x ² -y ² , x ² -y ²)
T	3	0	0	-1	(R _x , R _y , R _z) (x, y, z)	(xy, xz, yz)

T _h	E	4C ₃	4C ₃ ²	3C ₂	i	4S ₆	4S ₆ ⁵	3 h		=exp(2 i/3)
A _g	1	1	1	1	1	1	1	1		x ² +y ² +z ²
A _u	1	1	1	1	-1	-1	-1	-1		
E _g	{1 1	*	*	{1 1	1	*	*	1		(2z ² -x ² -y ² , x ² -y ²)
E _u	{1 1	*	*	{1 1	-1	-	-	{-1 -1}		
T _g	3	0	0	-1	1	0	0	-1	(R _x , R _y , R _z)	
T _u	3	0	0	-1	-1	0	0	1	(x, y, z)	(xy, xz, yz)

T _d	E	8C ₃	3C ₂	6S ₄	6 d		
A ₁	1	1	1	1	1		x ² +y ² +z ²
A ₂	1	1	1	-1	-1		
E	2	-1	2	0	0		(2z ² -x ² -y ² , x ² -y ²)
T ₁	3	0	-1	1	-1	(R _x , R _y , R _z)	
T ₂	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

O	E	6C ₄	3C ₂ (=C ₄ ²)	8C ₃	6C ₂		
A ₁	1	1	1	1	1		x ² +y ² +z ²
A ₂	1	-1	1	1	-1		
E	2	0	2	-1	0		(2z ² -x ² -y ² , x ² -y ²)
T ₁	3	1	-1	0	-1	(R _x , R _y , R _z) (x, y, z)	
T ₂	3	-1	-1	0	1		(xy, xz, yz)

