Shortcomings of Teaching Chemical Group Theory with a Limited Use of Linear Algebra

A Thesis
Presented in Partial Fulfillment of the Requirements for the
Degree of Master of Science
with a
Major in Chemistry
in the
College of Graduate Studies
University of Idaho
by
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August 2017

AUTHORIZATION TO SUBMIT THESIS

This thesis of Nichole R. Valdez, submitted for the degree of Master of Science with a Major in Chemistry and titled “Shortcomings of Teaching Chemical Group Theory with a Limited Use of Linear Algebra,” has been reviewed in final form. Permission, as indicated by the signatures and dates below, is now granted to submit final copies to the College of Graduate Studies for approval.

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ABSTRACT

Several textbooks on chemical group theory were examined and showed a wide range of inconsistencies in content. Many authors attempt to make their texts student-friendly by stripping out linear algebra concepts and focusing instead on visualizations of symmetry operations. This inevitably leads to an incomplete understanding of how to apply group theory to chemistry, and the lack of a standard across texts can lead a student who is using multiple sources to come to an incorrect conclusion. A guide was crafted to provide continuity across previously published group theory texts and to fill in the missing linear algebra concepts. It contains explanations of how to derive the rotation matrices for both clockwise and anticlockwise rotation, as well as reflection, inversion, and improper rotation. In addition, the guide shows how to derive a character table and includes the matrices for symmetry operations organized by principal rotation axis.

ACKNOWLEDGEMENTS

I would like to thank Dr. Mickey Gunter for providing the funding necessary to complete a Ph.D. in mineralogy and Dr. Thomas Bitterwolf for encouraging me to put my graduate chemistry courses to use outside of the geology department. I am grateful to the chairs of both departments for making the simultaneous degrees possible.

A large portion of this work would not have been possible without the chemistry students of the 2017 Group Theory course. Thank you for bearing with me as a first-time instructor, and for bravely facing advanced group theory topics while I enthusiastically presented them. Special recognition goes to Margaux Birdsall for bringing the B_3 irreducible representation to my attention. I hope Part III of this thesis provides some explanation of the confusing notation.

For Mindy

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CHAPTER ONE: INTRODUCTION TO TEACHING GROUP THEORY IN CHEMISTRY

1.1 The history of group theory in chemistry

Group theory is a branch of mathematics that is used to study systems where symmetry is present (Weisstein, 2017a). These systems can be abstract, or group theory can be applied to physical systems. When group theory is applied to chemistry, a chemist can mathematically describe the symmetry of molecules, determine bonding orbitals, and calculate vibrational modes. The symmetry of a molecule is described by using a center of symmetry, which may be an atom, a bond, or a point in space. Because of this fixed point of symmetry, the mathematical groups that are used to describe molecules are called point groups. The properties of each point group can be summarized into a character table, and chemists use this character table to determine bonding.

F. Albert Cotton (1990) provides a concise definition of a mathematical group where, "a group is a collection of elements that are interrelated according to certain rules." Elements here does not mean chemical elements, but rather symmetry operations. A symmetry operation will leave a molecule indistinguishable (but not identical) upon completion. For example, an ammonia molecule will be indistinguishable before and after rotation of 120° or 240° about an axis through the nitrogen atom. Other such symmetry operations include reflection across a mirror plane and inversion through the center of symmetry.

Group Theory was developed throughout the early 19th century by a number of prominent mathematicians, and was not brought into the field of chemistry until the turn of the century (Bishop, 1973). Group theory was given its name by Évariste Galois [1811-32], who is generally considered to be the first to develop the theory, even though Carl Friedrich Gauss [1777-1855] worked on the concepts earlier without publishing the results (Weisstein, 2017). Augustin Louis Cauchy [1787-1857] expanded on Galois' groups and developed the theory of permutation groups (Bishop, 1973). A permutation group is different than an abstract (Galois) group in that Cauchy applied group theory (as Galois and contemporaries knew it) to positions, such as points in a Cartesian system. Arthur Cayley [1821-95] then unified the work on groups by Galois, Cauchy, and others in his 1854 paper, *On the theory of groups, as* *depending on the symbolic equation* $\theta^n = 1$. This paper gives a definition for the abstract (finite) group, which is still used in modern times, as, "a set of symbols, all of them different, and such that the product of any two of them (no matter in what order), or the product of any one of them into itself belongs to the set, is said to be a group" (Cauchy, 1854). In point group symmetry, this can be visualized as combining two quarter rotations to get one half rotation. Both the quarter rotation and the half rotation must be in the same group.

Group theory was brought into chemistry by the advent of character tables, which allowed all of the symmetry elements to be combined and simplified into a more usable tool. This was enabled by two fundamental developments by Ferdinand Georg Frobenius [1849-1917]. Frobenius first applied abstract group theory to vector spaces, which allowed the members of a group to be written as linear transformations using matrices in what is known as group representation (see Rowland, 2017). The symmetry operations, in matrix form, could then be grouped together as classes by using the trace of each matrix. Symmetry elements that are in the same class of the same group will have the same trace, or group character (Weisstein, 2017b). A direct example of using vector spaces to develop a character table for a chemical compound is given in Chapter III.

Group theory was almost immediately applied to the newly emerging field of quantum mechanics in the mid 1920s. Werner Heisenberg [1901-1976] and others introduced matrices with infinite rows and columns to model position and momentum coordinates for a given particle (Wigner, 1959). Hermann Weyl [1885-1955] had been working with infinite groups of this type, called continuous groups, and their new use in quantum mechanics led him to write a book in 1928 that put group theory "in a form suitable to the requirements of quantum physics" (Weyl, 1950). Eugene Wigner [1902-1995] further developed quantum mechanics concepts and received half of the 1963 Nobel Prize in physics "for his contributions to the theory of the atomic nucleus and the elementary particles, particularly through the discovery and application of fundamental symmetry principles" (Nobel Media, 2014a).

It was also of interest during this time to use symmetry to characterize bonding, and through this interest molecular orbital theory and crystal field theory were developed. Molecular orbital theory was developed by Robert S. Mulliken [1896-1986] and Friedrich Hund [1896-1997], and assigns electrons to overlapping orbitals in a molecule (as opposed to specific bonds) in the same way that electrons are assigned to atomic orbitals in a free atom. The notation seen in point group tables alongside each irreducible representation is known as Mulliken notation (Mulliken, 1933). Mulliken went on to win the 1966 Nobel Prize in Chemistry "for his fundamental work concerning chemical bonds and the electronic structure of molecules by the molecular orbital method" (Nobel Media, 2014b). However, it was Hund who used quantum mechanics to compare the spectra of atoms and diatomic molecules to provide much of this insight, and Mulliken himself referred to molecular orbital theory as Hund-Mulliken theory (Mulliken, 1966).

Crystal field theory was developed when Hans Albrecht Bethe [1906-2005] used group theory to show how electronic configurations that are equivalent (degenerate) in a free atom change when constrained by symmetry in a lattice (Bethe, 1929). Bethe's paper was particularly exciting to John Hasbrouck Van Vleck [1899-1980] and his students (Anderson, 1987), who then worked with a similar method (Van Vleck, 1932). Bethe's crystal field theory was limited by treating the interaction between metal ions and ligands as purely electrostatic until Van Vleck showed that the method would still work for compounds with semi-covalent bonding (Van Vleck, 1935; Cotton, 1990). Van Vleck did this in a magnetism paper by investigating iron cyanide complexes, which have uncharacteristically low susceptibility due to large interatomic forces. These interatomic forces could be accounted for with both crystal field theory and molecular orbital theory. The combination of elements from both techniques became known as ligand-field theory, which is still used today by chemists who employ group theory.

1.2 Teaching group theory to chemistry students

Group theory has a rich developmental history in mathematics, and elements of group properties are taught in both introductory and advanced abstract algebra courses to students with a strong mathematical background. There is, however, no singular way to teach applied group theory, and chemistry instructors are faced with the difficult task of teaching to students of a mixed mathematical background. Furthermore, some instructors do not have a strong linear algebra or abstract algebra background themselves. Because of this, authors of chemistry textbooks often attempt to present group theory with as little math as possible. The visual component of symmetry elements and operations is crucial for understanding symmetry, but often it is presented alone. When an explanation of linear algebra is stripped away, students are left to rely on using character tables that they never fully understand. In most cases, a student can get as far as they need to go for a segment of an inorganic chemistry course without understanding these principles, but they are unlikely to return to group theory later in their undergraduate or graduate studies when a better understanding would be most helpful.

The lack of a standard for teaching group theory to chemists results not only in inconsistencies between the level of mathematical devotion, but also in the content itself. The three most notable differences were 1) the specified direction of rotation about a symmetry axis, 2) whether the derivation of a character table was explained, and 3) whether d-orbital bonding was discussed.

1.3 Inconsistencies between group theory texts

1.3.1 Rotation about a symmetry axis

A molecule with a symmetry rotation axis will be symmetrical whether it is rotated clockwise or anticlockwise. The decision of which to use is arbitrary, but must be consistent. In cases where mathematics is left out, the reasons why are invisible. However, if the general rotation matrices for clockwise and anticlockwise rotation are derived, one can see that they are different. Because of this, a rotation matrix for a specific *n*-fold rotation presented in one textbook may be different than that that found in a different textbook, which makes it difficult for a student to compare two sources. Furthermore, the way in which the rotation matrix is applied (horizontal or vertical) has consequences in linear algebra that can leave two clockwise rotation sources incomparable. This is discussed in great detail in Chapter Two where a guide to the matrices used in chemical group theory is presented. A darker consequence of the inconsistent principal rotation direction, and of avoiding mathematics in general, can be seen in some published textbooks, where the rotation matrix that is presented is incorrect. The guide will prepare the student to identify these inaccuracies. An example of one such inaccuracy is presented to the reader of this thesis in Chapter Four.

Table 1.3.1 shows the variation in choice of matrices across all textbooks examined. The ISBN column indicates The International Serial Book Number or the Library of Congress Catalog Card Number (LCCN) of each source. These are included in the reference list at the end of the chapter. The Written Direction column indicates what the author stated was the principal rotation direction. The Diagram Direction indicates which direction the arrows were drawn on rotation diagrams in each book. The Rotation Matrix column indicates which direction the rotation matrix will rotate the original vectors. The matrix orientation column indicates whether the rotation matrix is formatted to be horizontal (row matrix) $[X\ Y\ Z]$ or vertical (column matrix) $\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$.

Table 1.3.1 Principal Rotation Axis and Given Matrices

ISBN	Principal Rotation Axis				
	Axis	Written Direction	Diagram Direction	Rotation Matrix	Matrix Orientation
019855866X	N/A	Both	Both	N/A	N/A
199541423	Z	Both	Anticlockwise	Anticlockwise	Horizontal
0486673553	Z	Clockwise	Clockwise	Both	Vertical
9812530974	Z	Both	Anticlockwise	Clockwise*	Vertical
0121729508	Z	Clockwise	N/A	Clockwise	Vertical
6311428	Z	N/A	Anticlockwise	Clockwise	Vertical
0471510949	Z	N/A	Anticlockwise	Both*	Vertical
0444201149	Z	Clockwise	Clockwise	Clockwise	Vertical
0333492986	Z	Clockwise	Clockwise	Clockwise	Both
0486783146	Z	Both	N/A	Clockwise	Vertical
6828096	Z	Both	Both	N/A	N/A
3540541268	Z	N/A	N/A	NA	NA
6913607	Z	N/A	Anticlockwise	Anticlockwise	Vertical
0486661814	Z	N/A	N/A	Clockwise	Vertical
805337911	Z	N/A	N/A	Clockwise	Vertical
41209570X	Z	Clockwise	Clockwise	Clockwise	Horizontal
521642507	Z	Anticlockwise	Anticlockwise	Clockwise*	Vertical
6425890	Z	Clockwise	Anticlockwise	Both	Vertical
0470060407	Z	Both	Both	Anticlockwise	Horizontal

0935702997	Z	N/A	Anticlockwise	Clockwise*	Vertical
0486421827	Z	Anticlockwise	Anticlockwise	Anticlockwise	Horizontal
0857092403	Z	N/A	Both	Clockwise	Vertical
125083475	Z	N/A	N/A	Clockwise	Vertical
136153836	Z	Anticlockwise	Anticlockwise	Clockwise*	Vertical
0486681947	N/A	N/A	N/A	N/A	N/A
6520161	Z	Unclear	Anticlockwise	Clockwise	Horizontal
716736241	Z	N/A	Clockwise	N/A	N/A
048645035X	Z	N/A	Anticlockwise	Both*	Vertical
0471489399	Z	N/A	Clockwise	Both	Vertical
019855964X	Z	Clockwise	Clockwise	Clockwise	Clockwise
0486602691	N/A	N/A	N/A	N/A	N/A
5910741	N/A	N/A	N/A	N/A	N/A

* Seemingly unintentional

The number of textbooks that define the principal rotation direction as clockwise is almost equal to the number of textbooks that define it as anticlockwise. In most cases, this stated direction lines up with what the rotation matrix provides. In the cases where it does not, there seems to be either a typographical error or an incorrect matrix that propagates through the chapter. The majority of authors prefer the rotation matrix to be set up for a transformation on a column matrix. There is sometimes an inconsistency between what the author states is the principal rotation direction and which way the arrows are drawn in rotation diagrams, but this is a relatively minor inconvenience in comparison.

1.3.2 Derivation of character tables

Of the textbooks examined, about half dedicated a section to discussing how a character table is derived. Without an explanation of this type, a student will not fully understand the characters they are using when simplifying reducible representations. The character table for the C_{3v} point group is derived for the student in Chapter Four.

Table 1.3.2 shows the textbooks that were examined and whether the derivation of character tables was included.

Table 1.3.2 Character Tables and d-orbital Bonding

ISBN	Deriv. Char. Tables	d-orbital reducibles
019855866X	No	No
199541423	No	No
0486673553	Yes	Yes
9812530974	Yes	Yes
0121729508	No	No
6311428	Yes	Yes
0471510949	Yes	Yes
0444201149	Yes	Yes
0333492986	Yes	Yes
0486783146	Yes	No
6828096	No	Yes
3540541268	No	No
6913607	No	Yes
0486661814	No	No
805337911	No	Yes
41209570X	No	No
521642507	No	No
6425890	Yes	Yes
0470060407	No	Yes
0935702997	No	No
0486421827	Yes	No
0857092403	Yes	Yes
125083475	Yes	No
136153836	Yes	hybrid only
0486681947	No	No
6520161	No	Yes
716736241	No	No
048645035X	Yes	Yes
0471489399	No	No
019855964X	Yes	No
0486602691	No	No
5910741	No	No

1.3.3 Discussion of d-orbital bonding

Another subject that is not often included is bonding with d-orbitals. As group theory is usually taught in inorganic chemistry courses, the exclusion of more complex reducible representations limits the student to only simple bonding calculations with s and p orbitals. The number of books that include a discussion of d-orbital bonding is about equal to the number of books that do not include d-orbital bonding. The presence or absence of a d-orbital bonding section in all sources is indicated in **Table 1.3.2**.

CHAPTER ONE REFERENCES

Bethe, H. A. Termaufspaltung in Kristallen [Splitting of Terms in Crystals. Translated by Consultants Bureau, New York]. Ann. Phys., **1929**, 3, 133-208.

Bishop, D.M. *Group Theory and Chemistry*; Dover Publications, Inc.: New York, **1973**. ISBN 0486673553.

Cayley, A. On the theory of groups, as depending on the symbolic equation $\theta^n = 1$. *Phil. Mag.*, 4th Series. **1854**, 7, 40-47.

Cotton, F.A. *Chemical Applications of Group Theory*, 3rd Ed.; John Wiley and Sons, Inc.: New York, **1990**. ISBN 0471510949.

Mulliken, R.S. Electronic Structures of Polyatomic Molecules and Valence. IV. Electronic States, Quantum Theory of the Double Bond. Phys. Rev. **1933**, 43, 279-302.

Mulliken, R.S. Nobel Lecture December 12, **1966**: Spectroscopy, molecular orbitals, and chemical bonding. *In Nobel Lectures: Chemistry 1963-1970*; World Scientific: River Edge, NJ, 1999. ISBN 9810234082.

Nobel Media. The Nobel Prize in Physics 1963, **2014a**. Nobelprize.org. https://www.nobelprize.org/nobel_prizes/physics/laureates/1963 (accessed April 27, 2017).

Nobel Media. The Nobel Prize in Chemistry 1966, **2014b**. Nobelprize.org. http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1966 (accessed April 29, 2017).

Rowland, T. Group Representation, **2017**. Wolfram MathWorld. http://mathworld.wolfram.com/GroupRepresentation.html (accessed April 27, 2017).

Van Vleck, J.H. *The theory of electric and magnetic susceptibilities*. Clarendon Press: Oxford, **1932**. ISBN

Van Vleck, J.H. Valence Strength and the Magnetism of Complex Salts. *J. Chem. Phys*. **1935**, 3, 807- 813. DOI 10.1063/1.1749596.

Weisstein, E.W. Group Theory, **2017a**. Wolfram MathWorld. http://mathworld.wolfram.com/GroupTheory.html (accessed April 27, 2017).

Weisstein, E.W. Group character, **2017b**. Wolfram MathWorld. http://mathworld.wolfram.com/GroupCharacter.html (accessed April 27, 2017).

Weyl, H. *The Theory of Groups & Quantum Mechanics*. Dover Publications, Inc.: New York, **1950**. ISBN 0486602699.

Wigner, E.P. Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra. Academic Press: New York, **1959**. LOCCCN 59-10741.

TABLE 1.3.1 AND TABLE 1.3.2 REFERENCES

Altmann, S.L. *Band Theory of Solids: An Introduction From the Point of View of Symmetry*; Clarendon Press: Oxford, 1994. ISBN 019855866X.

Atkins, P. and Friedman, R. *Molecular Quantum Mechanics*, 5th Ed.; Oxford University Press: New York, 2011. ISBN 0199541423.

Bishop, D.M. *Group Theory and Chemistry*; Dover Publications, Inc.: New York, 1973. ISBN 0486673553.

Carter, R.L. *Molecular Symmetry and Group Theory*; John Wiley and Sons: New York, 2005. ISBN 9812530975.

Chisholm, C.D.H. *Group Theoretical Techniques in Quantum Chemistry*; Academic Press: London, 1976. ISBN 0121729508.

Cotton, F.A. *Chemical Applications of Group Theory*; John Wiley and Sons: New York, 1963. LCCCN 63-11428.

Cotton, F.A. *Chemical Applications of Group Theory*, 3rd Ed.; John Wiley and Sons, Inc.: New York, 1990. ISBN 0471510949.

Davidson, G. *Introductory Group Theory for Chemists*; Applied Science Publishers, Ltd.: London, 1971. ISBN 0444201149.

Davidson, G. *Group Theory for Chemists*; Macmillan Press Ltd.: London, 1993. ISBN 0333492986.

Duffy, G.H. *Applied Group Theory for Physicists and Chemists*; Dover Publications, Inc.: New York, 1992.

Ferraro, J.R. and Ziomek, J.S. *Introductory Group Theory and Its Application to Molecular Structure*; Plenum Press: New York, 1969. LCCCN 68-28096.

Fujita, S. *Symmetry and Combinatorial Enumeration in Chemistry*; Springer-Verlag: Germany. 1991. ISBN 3540541268.

Hall, L.H. *Group Theory and Symmetry in Chemistry*; McGraw-Hill, Inc.: USA, 1969. LOCCCN 69-13607.

Hamermesh, M. *Group Theory and its Application to Physical Problems*; Dover Publications, Inc.: New York, 1962. ISBN 0486661814.

Hatfield, W.E. and Palmer, R.A. Problems in Structural Inorganic Chemistry; W.A. Benjamin, Inc.: New York, 1971.

Hollas, J.M. *Symmetry in Molecules*; William Clowes & Sons, Ltd.: London, 1972. ISBN 41209570X.

Jacobs, P. *Group Theory with Applications in Chemical Physics*; Cambridge University Press: New York, 2005. ISBN 0521642507.

Jaffé, H.H. and Orchin, M. *Symmetry in Chemistry*; John Wiley & Sons, Inc.: New York, 1965. LCCCN 64-25890.

Kettle, F.A.S. *Symmetry and Structure: Readable Group Theory for Chemists*, 3rd Ed.; John Wiley & Sons, Inc.: West Sussex, 2007. ISBN 0470060407.

McQuarrie, D.A. and Simon, J.D. *Physical Chemistry: A Molecular Approach*; University Science Books: Sausalito, CA, 1997. ISBN 0935702997.

McWeeny, R. *Symmetry: An Introduction to Group Theory and Its Applications*; Dover Publications, Inc.: New York, 2002. ISBN 0486421821.

Molloy, K.C. Group Theory for Chemists: Fundamental Theory and Applications, 2nd Ed.; Woodhead Publishing: Philadelphia, 2013. ISBN 0857092403.

Mortimer, R.G. Mathematics for Physical Chemistry, 3rd Ed.; Elsevier Academic Press: Burlington, MA, 2005. ISBN 0125083475.

Miessler, G.L. and Tarr, D.A. *Inorganic Chemistry*, 4th Ed.; Pearson Prentice Hall: New York, 2010. ISBN 0136153836.

Molloy, K.C. *Group Theory for Chemists: Fundamental Theory and Applications*, 2nd Ed.; Woodhead Publishing: Philadelphia, 2013. ISBN 0857092403

Mortimer, R.G. *Mathematics for Physical Chemistry*, 3rd Ed.; Elsevier Academic Press: Burlington, MA, 2005. ISBN 0125083475.

Miessler, G.L. and Tarr, D.A. Inorganic Chemistry, 4th Ed.; Prentice Hall: New York, 2011. ISBN 0136128661.

Rose, J.S. A Course on Group Theory; Dover Publications, Inc.; New York, 1978. ISBN 0486681947.

Schonland, D.S. *Molecular Symmetry: An Introduction to Group Theory and its Uses in Chemistry*; D. Van Nostrand Company Ltd.: London, 1965. LOCCCN 65-20161.

Shriver, D. and Atkins, P. *Inorganic Chemistry*, 3rd Ed.; W.H. Freeman and Company: New York, 1999. ISBN 0716736241.

Tsukerblat, B.S. *Group Theory in Chemistry and Spectroscopy: A Simple Guide to Advanced Usage*; Dover Publications, Inc.: New York, 2006. ISBN 048645035X.

Vincent, A. *Molecular Symmetry and Group Theory*, 2nd Ed.; John Wiley & Sons, Inc.: New York, 2001. ISBN 0471489399.

Walton, P.H. *Beginning Group Theory for Chemistry*; Oxford University Press: New York, 1998. ISBN 019855964X.

Weyl, H. *The Theory of Groups & Quantum Mechanics*. Dover Publications, Inc.: New York, 1950. ISBN 0486602699.

Wigner, E.P. Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra. Academic Press: New York, 1959. LOCCCN 59-10741.

CHAPTER TWO: A GUIDE TO MATRICES USED IN CHEMICAL GROUP THEORY

2.1 Derivation of the anticlockwise rotation matrix

In the case of anticlockwise rotation, the black arrows are rotated left to the position of the blue arrows by an angle θ. The new position of X, X', and the new position of Y, Y', can be defined as the hypotenuse, H, of a right isosceles triangle with angle θ. X' can be expressed as the sum of two vectors (see **Figure 2.1.1**): the adjacent length, $\vec{A}$, and the opposite length, $\vec{O}$, which are some fraction of the length of X and Y, respectively*:

$$\vec{X'} = \vec{A} + \vec{O}$$

where $A = \frac{A}{H}H$ and $O = \frac{O}{H}H$

so $X' = \frac{A}{H}H + \frac{O}{H}H$

$\frac{A}{H}$ is the same as the cosine of θ and $\frac{O}{H}$ is the same as the sine of θ so:

X' can be written as: $X' = \cos\theta \cdot X + \sin\theta \cdot Y$

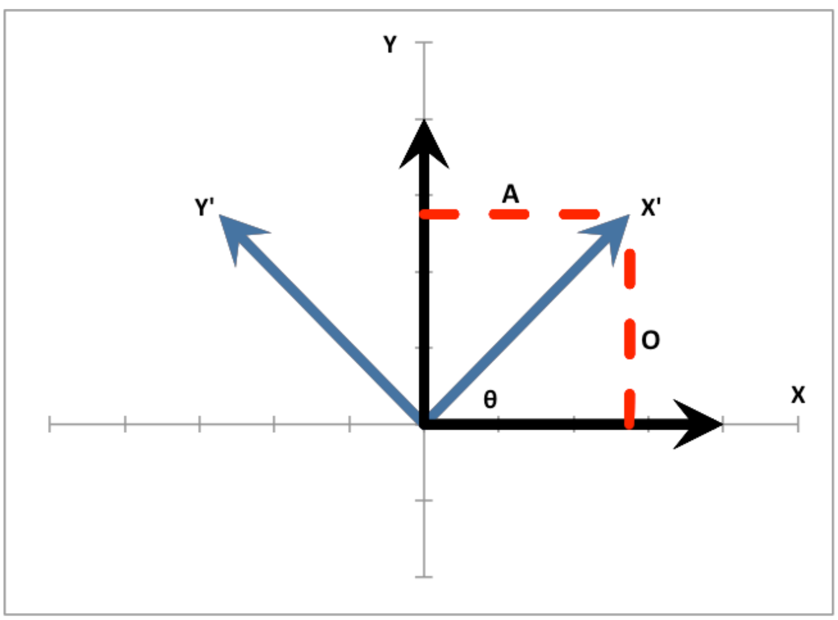

Figure 2.1.1 Anticlockwise Rotation Matrix for X'

*Vector notation arrows removed for ease of reading

Y' can be expressed as the sum of two vectors (see **Figure 2.1.2**): the opposite length, $\vec{O}$, and the adjacent length, $\vec{A}$, which are some fraction of the length of -X and Y, respectively:

$$\overrightarrow{Y'} = \vec{O} + \vec{A}$$

where $O = \frac{O}{H}H$ and $A = \frac{A}{H}H$

so $Y' = \frac{O}{H}H + \frac{A}{H}H$

$\frac{O}{H}$ is the same as the sine of θ and $\frac{A}{H}$ is the same as the cosine of θ so:

Y' can be written as: $Y' = -\sin\theta \cdot X + \cos\theta \cdot Y$

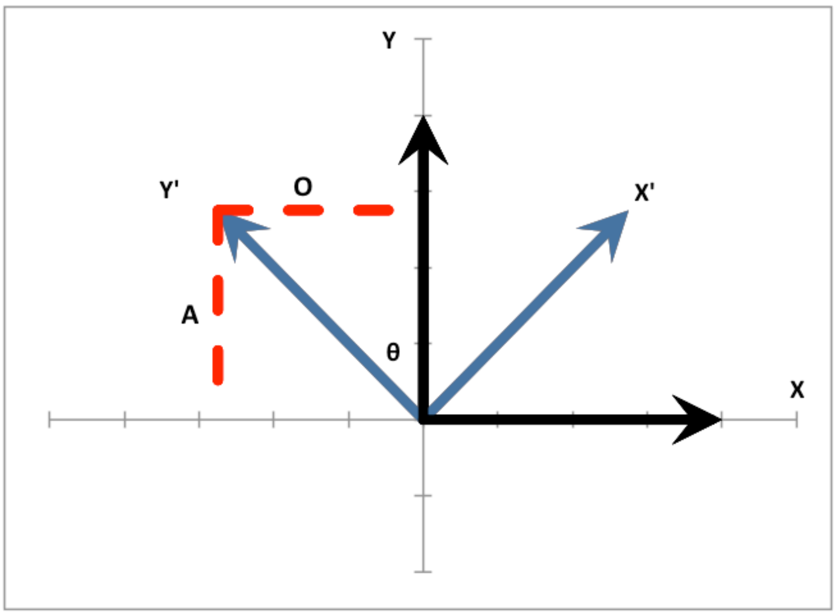

Figure 2.1.2 Anticlockwise Rotation Matrix for Y'

The vectors derived above are:

$X' = \cos\theta\, X + \sin\theta Y$

$Y' = -\sin\theta X + \cos\theta Y$

Put into matrix form:

$$\begin{bmatrix} X' \\ Y' \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix}$$

From this we get the anticlockwise (ACW) rotation matrix, R:

$$R_{ACW} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

An alternate form of the anticlockwise rotation matrix is as follows:

$$[X'Y'] = [X\,Y]\begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$$

$$R_{ACW} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$$

The matrices can be expanded to three dimensions with Z as the rotation axis with the following equations:

$$X' = \cos\theta\, X + \sin\theta Y$$

$$Y' = -\sin\theta X + \cos\theta Y$$

$$Z' = Z$$

$$\begin{bmatrix} X' \\ Y' \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}\begin{bmatrix} X \\ Y \end{bmatrix}$$

$$R_{ACW} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

$$R_{ACW} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Or

$$[X'Y'] = [X\,Y]\begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$$

$$R_{ACW} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$$

$$[X'Y'Z'] = [X\,Y\,Z]\begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$R_{ACW} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Note the column rotation matrix and the row rotation matrix are inverses of each other.

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

$$R_{ACW} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$[X'Y'Z'] = [X\ Y\ Z] \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$R_{ACW} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

2.2 Derivation of the clockwise rotation matrix

In the case of clockwise rotation, the black arrows are rotated right to the position of the blue arrows by an angle θ. The new position of X, X', and the new position of Y, Y', can be defined as the hypotenuse, H, of a right triangle with angle θ. X' can be expressed as the sum of two vectors (see **Figure 2.2.1**): the adjacent length, $\vec{A}$, and the opposite length, $\vec{O}$, which are some fraction of the length of X and -Y, respectively:

$$\vec{X'} = \vec{A} + \vec{O}$$

where $A = \frac{A}{H}H$ and $O = \frac{O}{H}H$

so $X' = \frac{A}{H}H - \frac{O}{H}H$

$\frac{A}{H}$ is the same as the cosine of θ and $\frac{O}{H}$ is the same as the sine of θ so:

X' can be written as: $X' = \cos\theta \cdot X - \sin\theta \cdot Y$

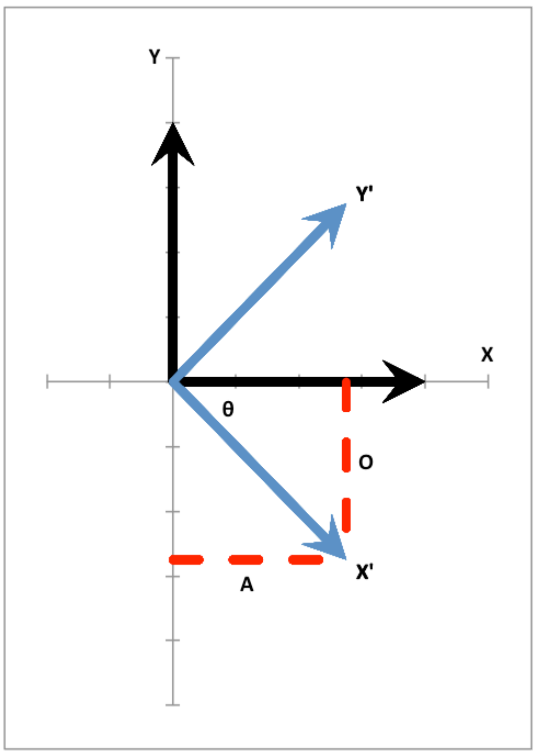

Figure 2.2.1 Clockwise Rotation Matrix for X'

Y' can be expressed as the sum of two vectors (see **Figure 2.2.2**): the opposite length, $\vec{O}$, and the adjacent length, $\vec{A}$, which are some fraction of the length of X and Y, respectively:

$$\vec{Y'} = \vec{O} + \vec{A}$$

where $O = \frac{O}{H}H$ and $A = \frac{A}{H}H$

so $Y' = \frac{O}{H}H + \frac{A}{H}H$

$\frac{O}{H}$ is the same as the sine of θ and $\frac{A}{H}$ is the same as the cosine of θ so:

Y' can be written as: $Y' = \sin\theta \cdot X + \cos\theta \cdot Y$

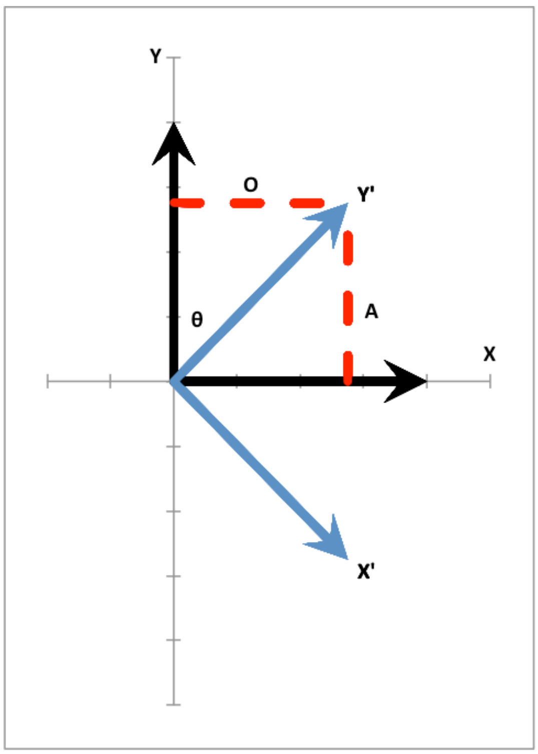

Figure 2.2.2 Clockwise Rotation Matrix for Y'

The vectors derived above are:

$X' = \cos\theta\, X - \sin\theta Y$

$Y' = \sin\theta X + \cos\theta Y$

Put into matrix form:

$$\begin{bmatrix} X' \\ Y' \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix}$$

From this we get the clockwise (CW) rotation matrix, R:

$$R_{CW} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$$

An alternate form of the clockwise rotation matrix is as follows:

$$[X'Y'] = [X\ Y] \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

$$R_{CW} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

The matrices can be expanded to three dimensions with Z as the rotation axis with the following equations:

$$X' = \cos\theta\, X - \sin\theta Y$$

$$Y' = \sin\theta X + \cos\theta Y$$

$$Z' = Z$$

$$\begin{bmatrix} X' \\ Y' \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix}$$

$$R_{CW} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$$

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

$$R_{CW} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Or

$$[X'\ Y'] = [X\ Y] \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

$$R_{CW} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

$$[X'Y'Z'] = [X\ Y\ Z]\begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$R_{CW} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Again note the column rotation matrix and the row rotation matrix are inverses of each other.

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

$$R_{CW} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$[X'Y'Z'] = [X\ Y\ Z]\begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$R_{CW} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

2.3 The four possible rotation matrices

The relationship between a rotation matrix and its inverse poses an additional problem that can lead to confusion. The anticlockwise column rotation matrix is the same as the clockwise row rotation matrix. Likewise, the clockwise column rotation matrix is the same as the anticlockwise row rotation matrix.

Anticlockwise

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

$$[X'Y'Z'] = [X\ Y\ Z]\begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Clockwise

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

$$[X'Y'Z'] = [X\ Y\ Z]\begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Anticlockwise $\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$

$$X' = \cos\theta\, X + \sin\theta X$$

$$Y' = -\sin\theta Y + \cos\theta Y$$

$$\begin{bmatrix} X' \\ Y' \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix}$$

$$R_{ACW} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

$$R_{ACW} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Anticlockwise [X Y Z]

$$X' = \cos\theta\, X + \sin\theta Y$$

$$Y' = -\sin\theta X + \cos\theta Y$$

$$[X'Y'] = [X\ Y] \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$$

$$R_{ACW} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$$

$$[X'Y'] = [X\ Y\ Z] \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$R_{ACW} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Clockwise $\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$

$$X' = \cos\theta\, X - \sin\theta Y$$

$$Y' = \sin\theta X + \cos\theta Y$$

$$\begin{bmatrix} X' \\ Y' \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix}$$

$$R_{CW} = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$$

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

$$R_{CW} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Clockwise [X Y Z]

$$X' = \cos\theta\, X - \sin\theta Y$$

$$Y' = \sin\theta X + \cos\theta Y$$

$$[X'Y'] = [X\ Y] \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

$$R_{CW} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

$$[X'Y'] = [X\ Y] \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$R_{CW} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Note that the clockwise matrix can be used for an anticlockwise rotation, and vise versa, if the angle is defined as negative. For example, an anticlockwise rotation of 60° corresponds to a clockwise rotation of 300°.

Anticlockwise 60° using an anticlockwise matrix:

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos 60 & \sin 60 & 0 \\ -\sin 60 & \cos 60 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

Clockwise 300° using an anticlockwise matrix:

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos -300 & \sin -300 & 0 \\ -\sin -300 & \cos -300 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

2.4 Other generalized matrix operations

Reflections

$$\sigma_{v(XZ)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_{v(YZ)} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_{v(XY)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$\sigma_{d} = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_{d} = \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_{h} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Inversion

$$i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

The orientation of the matrix does not matter for rotation and inversion. The matrices provided above can transform a row matrix, [X Y Z], or column matrix, $\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$.

Improper rotations are found by multiplying the rotation matrix by the horizontal mirror plane. The order of multiplication does not matter for the S_n operation.

Improper Rotations

Anticlockwise [X Y Z]

$$S_{n(ACW)} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Clockwise [X Y Z]

$$S_{n(CW)} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Anticlockwise $\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$

$$S_{n(ACW)} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Clockwise $\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$

$$S_{n(CW)} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Some texts may use an inversion matrix instead:

Anticlockwise [X Y Z]

$$S_{n(ACW)} = \begin{bmatrix} \cos(\theta+\pi) & -\sin(\theta+\pi) & 0 \\ \sin(\theta+\pi) & \cos(\theta+\pi) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Clockwise [X Y Z]

$$S_{n(CW)} = \begin{bmatrix} \cos(\theta+\pi) & \sin(\theta+\pi) & 0 \\ -\sin(\theta+\pi) & \cos(\theta+\pi) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Anticlockwise $\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$

$$S_{n(ACW)} = \begin{bmatrix} \cos(\theta+\pi) & \sin(\theta+\pi) & 0 \\ -\sin(\theta+\pi) & \cos(\theta+\pi) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Clockwise $\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$

$$S_{n(CW)} = \begin{bmatrix} \cos(\theta+\pi) & -\sin(\theta+\pi) & 0 \\ \sin(\theta+\pi) & \cos(\theta+\pi) & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

CHAPTER THREE: AN INDEX OF MATRICES ORDERED BY PRINCIPAL ROTATION AXIS

3.1 Low symmetry groups

C_1

$$\mathrm{E} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

C_s

E and one mirror plane only

C_i

E and inversion only

$$i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

3.2 C_2

C_2

θ	**sinθ**	**cosθ**
0	0	1
180	0	-1
360	0	1

Rotations

Anticlockwise [XYZ]

$C_2^1 = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$ $C_2^1 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

$X' = \cos(180°)X + \sin(180°)Y$

$X' = -1X + 0Y$

$Y' = -\sin(180°)X + \cos(180°)Y$

$Y' = 0X - 1Y$

$C_2^2 = E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$ $C_2^2 = E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

$X' = \cos(0°)X + \sin(0°)Y$

$X' = 1X + 0Y$

$Y' = -\sin(0°)X + \cos(0°)Y$

$Y' = 0X + 1Y$

Clockwise [XYZ]

$C_2^1 = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$ $C_2^1 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

$X' = \cos(180°)X - \sin(180°)Y$

$X' = -1X - 0Y$

$Y' = \sin(180°)X + \cos(180°)Y$

$Y' = 0X - 1Y$

$C_2^2 = E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$ $C_2^2 = E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

$X' = \cos(0°)X - \sin(0°)Y$

$$X' = 1X - 0Y$$

$$Y' = \sin(0°)X + \cos(0°)Y$$

$$Y' = 0X + 1Y$$

Reflections

$$\sigma_{v(XZ)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_{v(YZ)} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

3.3 C_3

C_3		
θ	**sinθ**	**cosθ**
120	$\sqrt{3}/_2$	$-{}^1/_2$
240	$-\sqrt{3}/_2$	$-{}^1/_2$

Rotations

Anticlockwise [XYZ]

$$C_3^1 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \quad C_3^1 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(120°)X + \sin(120°)Y$$

$$X' = -\frac{1}{2}X + \frac{\sqrt{3}}{2}Y$$

$$Y' = -\sin(120°)X + \cos(120°)Y$$

$$Y' = -\frac{\sqrt{3}}{2}X - \frac{1}{2}Y$$

$$C_3^2 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \quad C_3^2 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(240°)X + \sin(240°)Y$$

$$X' = -\frac{1}{2}X - \frac{\sqrt{3}}{2}Y$$

$$Y' = -\sin(240°)X + \cos(240°)Y$$

$$Y' = \frac{\sqrt{3}}{2}X - \frac{1}{2}Y$$

$$C_3^3 = E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad C_3^3 = E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(0°)X + \sin(0°)Y$$

$$X' = 1X + 0Y$$

$$Y' = -\sin(0°)X + \cos(0°)Y$$

$$Y' = 0X + 1Y$$

Clockwise [XYZ]

$\mathrm{C}_3^1 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$ $\mathrm{C}_3^1 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$

$$\mathrm{X}' = \cos(120°)\mathrm{X} - \sin(120°)\mathrm{Y}$$

$$\mathrm{X}' = -\tfrac{1}{2}\mathrm{X} - \tfrac{\sqrt{3}}{2}\mathrm{Y}$$

$$\mathrm{Y}' = \sin(120°)\mathrm{X} + \cos(120°)\mathrm{Y}$$

$$\mathrm{Y}' = \tfrac{\sqrt{3}}{2}\mathrm{X} - \tfrac{1}{2}\mathrm{Y}$$

$\mathrm{C}_3^2 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$ $\mathrm{C}_3^2 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$

$$\mathrm{X}' = \cos(240°)\mathrm{X} - \sin(240°)\mathrm{Y}$$

$$\mathrm{X}' = -\tfrac{1}{2}\mathrm{X} + \tfrac{\sqrt{3}}{2}\mathrm{Y}$$

$$\mathrm{Y}' = \sin(240°)\mathrm{X} + \cos(240°)\mathrm{Y}$$

$$\mathrm{Y}' = -\tfrac{\sqrt{3}}{2}\mathrm{X} - \tfrac{1}{2}\mathrm{Y}$$

$\mathrm{C}_3^3 = \mathrm{E} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$ $\mathrm{C}_3^3 = \mathrm{E} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

$$\mathrm{X}' = \cos(0°)\mathrm{X} - \sin(0°)\mathrm{Y}$$

$$\mathrm{X}' = 1\mathrm{X} - 0\mathrm{Y}$$

$$\mathrm{Y}' = \sin(0°)\mathrm{X} + \cos(0°)\mathrm{Y}$$

$$\mathrm{Y}' = 0\mathrm{X} + 1\mathrm{Y}$$

Reflections

Anticlockwise [XYZ]

$\sigma_{\mathrm{v}=} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$ $\sigma_{\mathrm{v}} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

X rotates 0°, Y rotates 180°

$$\mathrm{X}' = \cos(0°)\mathrm{X} + \sin(0°)\mathrm{Y}$$

$$\mathrm{X}' = 1\mathrm{X} + 0\mathrm{Y}$$

$$\mathrm{Y}' = -\sin(180°)\mathrm{X} + \cos(180°)\mathrm{Y}$$

$$\mathrm{Y}' = 0\mathrm{X} - 1\mathrm{Y}$$

$$\sigma_v = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix} \quad \sigma_v = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

X rotates 120° ACW (240° CW), Y rotates 300° ACW (60° CW)

$$X' = \cos(120°)X + \sin(120°)Y$$

$$X' = -\frac{1}{2}X + \frac{\sqrt{3}}{2}Y$$

$$Y' = -\sin(300°)X + \cos(300°)Y$$

$$Y' = \frac{\sqrt{3}}{2}X + \frac{1}{2}Y$$

$$\sigma_v = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix} \quad \sigma_v = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

X rotates 240° ACW (or 120° CW), Y rotates 60° ACW (or 300° CW)

$$X' = \cos(240°)X + \sin(240°)Y$$

$$X' = -\frac{1}{2}X - \frac{\sqrt{3}}{2}Y$$

$$Y' = -\sin(60°)X + \cos(60°)Y$$

$$Y' = -\frac{\sqrt{3}}{2}X + \frac{1}{2}Y$$

Clockwise [XYZ]

$$\sigma_{v=} \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad \sigma_v = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

X rotates 0°, Y rotates 180°

$$X' = \cos(0°)X - \sin(0°)Y$$

$$X' = 1X - 0Y$$

$$Y' = \sin(180°)X + \cos(180°)Y$$

$$Y' = 0X - 1Y$$

$$\sigma_v = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix} \quad \sigma_v = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

X rotates 120° CW (or 240° CW), Y rotates 300° CW (or 60° ACW)

$$X' = \cos(120°)X - \sin(120°)Y$$

$$X' = -\frac{1}{2}X - \frac{\sqrt{3}}{2}Y$$

$$Y' = \sin(300°)X + \cos(300°)Y$$

$$Y' = -\frac{\sqrt{3}}{2}X + \frac{1}{2}Y$$

$$\sigma_v = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix} \quad \sigma_v = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

X rotates 240° CW (120° ACW), Y rotates 60° CW (300° ACW)

$$X' = \cos(240°)X - \sin(240°)Y$$

$$X' = -\frac{1}{2}X + \frac{\sqrt{3}}{2}Y$$

$$Y' = \sin(60°)X + \cos(60°)Y$$

$$Y' = \frac{\sqrt{3}}{2}X + \frac{1}{2}Y$$

3.4 C_4

C_4

θ	**sinθ**	**cosθ**
90	1	0
180	0	-1
270	-1	0

Rotations

Anticlockwise [XYZ]

$$C_4^1 = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \quad C_4^1 = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(90°)X + \sin(90°)Y$$

$$X' = 0X + 1Y$$

$$Y' = -\sin(90°)X + \cos(90°)Y$$

$$Y' - 1X - 0Y$$

$$C_4^2 = C_2 = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \quad C_4^2 = C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(180°)X + \sin(180°)Y$$

$$X' = -1X + 0Y$$

$$Y' = -\sin(180°)X + \cos(180°)Y$$

$$Y' = 0X - 1Y$$

$$C_4^3 = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \quad C_4^3 = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(270°)X + \sin(270°)Y$$

$$X' = 0X - 1Y$$

$$Y' = -\sin(270°)X + \cos(270°)Y$$

$$Y' = 1X + 0Y$$

$$C_4^4 = E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad C_4^4 = E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(0°)X + \sin(0°)Y$$

$$X' = 1X + 0Y$$

$$Y' = -\sin(0°)X + \cos(0°)Y$$

$$Y' = 0X + 1Y$$

Clockwise [XYZ]

$$C_4^1 = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix} \quad C_4^1 = \begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(90°)X - \sin(90°)Y$$

$$X' = 0X - 1Y$$

$$Y' = \sin(90°)X + \cos(90°)Y$$

$$Y' - 1X - 0Y$$

$$C_4^2 = C_2 = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \quad C_4^2 = C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(180°)X - \sin(180°)Y$$

$$X' = -1X + 0Y$$

$$Y' = \sin(180°)X + \cos(180°)Y$$

$$Y' = 0X - 1Y$$

$$C_4^3 = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \quad C_4^3 = \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(270°)X - \sin(270°)Y$$

$$X' = 0X + 1Y$$

$$Y' = \sin(270°)X + \cos(270°)Y$$

$$Y' = -1X + 0Y$$

$$C_4^4 = E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad C_4^4 = E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(0°)X - \sin(0°)Y$$

$$X' = 1X + 0Y$$

$$Y' = \sin(0°)X + \cos(0°)Y$$

$$Y' = 0X + 1Y$$

Reflections

$$\sigma_v = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_d = \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_d = \begin{bmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

3.5 C_5

C_5

θ	**sinθ**	**cosθ**
36	$\sqrt{\left(\frac{5}{8}-\frac{\sqrt{5}}{8}\right)} \approx 0.588$	$\frac{1}{4}\left(1+\sqrt{5}\right)$ or ≈ 0.809
72	$\sqrt{\left(\frac{5}{8}+\frac{\sqrt{5}}{8}\right)} \approx 0.951$	$\frac{1}{4}\left(\sqrt{5}-1\right)$ or ≈ 0.309
108	$\sqrt{\left(\frac{5}{8}+\frac{\sqrt{5}}{8}\right)} \approx 0.951$	$\frac{1}{4}\left(1-\sqrt{5}\right)$ or ≈ -0.309
144	$\sqrt{\left(\frac{5}{8}-\frac{\sqrt{5}}{8}\right)} \approx 0.588$	$\frac{1}{4}\left(-1-\sqrt{5}\right)$ or ≈ -0.809
216	$-\sqrt{\left(\frac{5}{8}-\frac{\sqrt{5}}{8}\right)} \approx -0.588$	$\frac{1}{4}\left(-1-\sqrt{5}\right)$ or ≈ -0.809
252	$-\sqrt{\left(\frac{5}{8}+\frac{\sqrt{5}}{8}\right)} \approx -0.951$	$\frac{1}{4}\left(1-\sqrt{5}\right)$ or ≈ -0.309
288	$-\sqrt{\left(\frac{5}{8}+\frac{\sqrt{5}}{8}\right)} \approx -0.951$	$\frac{1}{4}\left(\sqrt{5}-1\right)$ or ≈ 0.309
324	$-\sqrt{\left(\frac{5}{8}-\frac{\sqrt{5}}{8}\right)} \approx -0.588$	$\frac{1}{4}\left(1+\sqrt{5}\right)$ or ≈ 0.809

Rotations

Anticlockwise [XYZ]

$$C_5^1 = \begin{bmatrix} \cos 72 & -\sin 72 \\ \sin 72 & \cos 72 \end{bmatrix} \quad C_5^1 = \begin{bmatrix} \cos 72 & -\sin 72 & 0 \\ \sin 72 & \cos 72 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(72°)X + \sin(72°)Y$$

$$X' = \left[\frac{1}{4}\left(\sqrt{5}-1\right)\right]X + \sqrt{\left(\frac{5}{8}+\frac{\sqrt{5}}{8}\right)}\,Y$$

$$X' \approx 0.309\,X + 0.951\,Y$$

$$Y' = -\sin(72°)X + \cos(72°)Y$$

$$Y' = -\sqrt{\left(\frac{5}{8}+\frac{\sqrt{5}}{8}\right)}\,X + \left[\frac{1}{4}\left(\sqrt{5}-1\right)\right]Y$$

$$Y' \approx -\,0.951\,X + 0.309\,Y$$

$$C_5^2 = \begin{bmatrix} \cos 144 & -\sin 144 \\ \sin 144 & \cos 144 \end{bmatrix} \quad C_5^2 = \begin{bmatrix} \cos 144 & -\sin 144 & 0 \\ \sin 144 & \cos 144 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(144°)X + \sin(144°)Y$$

$$X' = \left[\frac{1}{4}\left(-1-\sqrt{5}\right)\right]X + \sqrt{\left(\frac{5}{8}-\frac{\sqrt{5}}{8}\right)}\,Y$$

$$X' \approx -0.809\,X + 0.588\,Y$$

$$Y' = -\sin(144°)X + \cos(144°)Y$$

$$Y' = -\sqrt{\left(\frac{5}{8}-\frac{\sqrt{5}}{8}\right)}\,X + \left[\frac{1}{4}\left(-1-\sqrt{5}\right)\right]Y$$

$$Y' \approx -\,0.588\,X - 0.809\,Y$$

$$C_5^3 = \begin{bmatrix}\cos 216 & -\sin 216\\ \sin 216 & \cos 216\end{bmatrix} \quad C_5^3 = \begin{bmatrix}\cos 216 & -\sin 216 & 0\\ \sin 216 & \cos 216 & 0\\ 0 & 0 & 1\end{bmatrix}$$

$$X' = \cos(216°)X + \sin(216°)Y$$

$$X' = \left[\frac{1}{4}\left(-1-\sqrt{5}\right)\right]X - \sqrt{\left(\frac{5}{8}-\frac{\sqrt{5}}{8}\right)}\,Y$$

$$X' \approx -0.809\,X - 0.588\,Y$$

$$Y' = -\sin(216°)X + \cos(216°)Y$$

$$Y' = \sqrt{\left(\frac{5}{8}-\frac{\sqrt{5}}{8}\right)}\,X + \left[\frac{1}{4}\left(-1-\sqrt{5}\right)\right]Y$$

$$Y' \approx 0.588\,X - 0.809\,Y$$

$$C_5^4 = \begin{bmatrix}\cos 288 & -\sin 288\\ \sin 288 & \cos 288\end{bmatrix} \quad C_5^4 = \begin{bmatrix}\cos 288 & -\sin 288 & 0\\ \sin 288 & \cos 288 & 0\\ 0 & 0 & 1\end{bmatrix}$$

$$X' = \cos(288°)X + \sin(288°)Y$$

$$X' = \left[\frac{1}{4}\left(\sqrt{5}-1\right)\right]X - \sqrt{\left(\frac{5}{8}-\frac{\sqrt{5}}{8}\right)}\,Y$$

$$X' \approx 0.309\,X - 0.951\,Y$$

$$Y' = -\sin(288°)X + \cos(288°)Y$$

$$Y' = \sqrt{\left(\frac{5}{8}-\frac{\sqrt{5}}{8}\right)}\,X + \left[\frac{1}{4}\left(\sqrt{5}-1\right)\right]Y$$

$$Y' \approx 0.951\,X + 0.309\,Y$$

$$C_5^5 = E = \begin{bmatrix}1 & 0\\ 0 & 1\end{bmatrix} \quad C_5^5 = E = \begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}$$

$$X' = \cos(0°)X + \sin(0°)Y$$

$$X' = 1X + 0Y$$

$$Y' = -\sin(0°)X + \cos(0°)Y$$

$$Y' = 0X + 1Y$$

Clockwise [XYZ]

$$C_5^1 = \begin{bmatrix} \cos 72 & \sin 72 \\ -\sin 72 & \cos 72 \end{bmatrix} \quad C_5^1 = \begin{bmatrix} \cos 72 & \sin 72 & 0 \\ -\sin 72 & \cos 72 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(72°)X - \sin(72°)Y$$

$$X' = \left[\frac{1}{4}\left(\sqrt{5} - 1\right)\right] X - \sqrt{\left(\frac{5}{8} + \frac{\sqrt{5}}{8}\right)}\, Y$$

$$X' \approx 0.309\, X - 0.951\, Y$$

$$Y' = \sin(72°)X + \cos(72°)Y$$

$$Y' = \sqrt{\left(\frac{5}{8} + \frac{\sqrt{5}}{8}\right)}\, X + \left[\frac{1}{4}\left(\sqrt{5} - 1\right)\right] Y$$

$$Y' \approx 0.951\, X = +\, 0.309\, Y$$

$$C_5^2 = \begin{bmatrix} \cos 144 & \sin 144 \\ -\sin 144 & \cos 144 \end{bmatrix} \quad C_5^2 = \begin{bmatrix} \cos 144 & \sin 144 & 0 \\ -\sin 144 & \cos 144 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(144°)X - \sin(144°)Y$$

$$X' = \left[\frac{1}{4}\left(-1 - \sqrt{5}\right)\right] X - \sqrt{\left(\frac{5}{8} - \frac{\sqrt{5}}{8}\right)}\, Y$$

$$X' \approx -0.809\, X - 0.588\, Y$$

$$Y' = \sin(144°)X + \cos(144°)Y$$

$$Y' = \sqrt{\left(\frac{5}{8} - \frac{\sqrt{5}}{8}\right)}\, X + \left[\frac{1}{4}\left(-1 - \sqrt{5}\right)\right] Y$$

$$Y' \approx 0.588\, X - 0.809\, Y$$

$$C_5^3 = \begin{bmatrix} \cos 216 & \sin 216 \\ -\sin 216 & \cos 216 \end{bmatrix} \quad C_5^3 = \begin{bmatrix} \cos 216 & \sin 216 & 0 \\ -\sin 216 & \cos 216 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(216°)X - \sin(216°)Y$$

$$X' = \left[\frac{1}{4}\left(-1 - \sqrt{5}\right)\right] X + \sqrt{\left(\frac{5}{8} - \frac{\sqrt{5}}{8}\right)}\, Y$$

$$X' \approx -0.809\, X + 0.588\, Y$$

$$Y' = \sin(216°)X + \cos(216°)Y$$

$$Y' = -\sqrt{\left(\frac{5}{8} - \frac{\sqrt{5}}{8}\right)}\, X + \left[\frac{1}{4}\left(-1 - \sqrt{5}\right)\right] Y$$

$$Y' \approx -0.588\, X - 0.809\, Y$$

$$C_5^4 = \begin{bmatrix} \cos 288 & \sin 288 \\ -\sin 288 & \cos 288 \end{bmatrix} \quad C_5^4 = \begin{bmatrix} \cos 288 & \sin 288 & 0 \\ -\sin 288 & \cos 288 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(288°)X - \sin(288°)Y$$

$$X' = \left[\frac{1}{4}\left(\sqrt{5} - 1\right)\right] X + \sqrt{\left(\frac{5}{8} - \frac{\sqrt{5}}{8}\right)}\, Y$$

$$X' \approx 0.309\, X + 0.951\, Y$$

$$Y' = \sin(288°)X + \cos(288°)Y$$

$$Y' = -\sqrt{\left(\frac{5}{8} - \frac{\sqrt{5}}{8}\right)}\, X + \left[\frac{1}{4}\left(\sqrt{5} - 1\right)\right] Y$$

$$Y' \approx -\, 0.951\, X + 0.309\, Y$$

$$C_5^5 = E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad C_5^5 = E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(0°)X - \sin(0°)Y$$

$$X' = 1X + 0Y$$

$$Y' = \sin(0°)X + \cos(0°)Y$$

$$Y' = 0X + 1Y$$

Reflections

$$\sigma_{v(XZ)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

3.6 C_6

C_6

θ	**sinθ**	**cosθ**
60	$\sqrt{3}/_2$	$^1/_2$
120	$\sqrt{3}/_2$	$-\,^1/_2$
180	0	-1
240	$-\sqrt{3}/_2$	$-\,^1/_2$
300	$-\sqrt{3}/_2$	$^1/_2$

Rotations

Anticlockwise [XYZ]

$$C_6^1 = \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$$

$$C_6^1 = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(60°)\,X + \sin(60°)Y$$

$$X' = \frac{1}{2}X + \frac{\sqrt{3}}{2}Y$$

$$Y' = -\sin(60°)X + \cos(60°)Y$$

$$Y' = -\frac{\sqrt{3}}{2}X + \frac{1}{2}Y$$

$$C_6^2 = C_3^1 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \quad C_3^1 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(120°)X + \sin(120°)Y$$

$$X' = -\frac{1}{2}X + \frac{\sqrt{3}}{2}Y$$

$$Y' = -\sin(120°)X + \cos(120°)Y$$

$$Y' = -\frac{\sqrt{3}}{2}X - \frac{1}{2}Y$$

$$C_6^3 = C_2^1 = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \quad C_2^1 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(180°)X + \sin(180°)Y$$

$$X' = -1X + 0Y$$

$$Y' = -\sin(180°)X + \cos(180°)Y$$

$$Y' = 0X - 1Y$$

$$C_6^4 = C_3^2 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \quad C_3^2 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(240°)X + \sin(240°)Y$$

$$X' = -\frac{1}{2}X - \frac{\sqrt{3}}{2}Y$$

$$Y' = -\sin(240°)X + \cos(240°)Y$$

$$Y' = \frac{\sqrt{3}}{2}X - \frac{1}{2}Y$$

$$C_6^5 = \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix} \quad C_3^2 = \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(300°)X + \sin(300°)Y$$

$$X' = \frac{1}{2}X - \frac{\sqrt{3}}{2}Y$$

$$Y' = -\sin(300°)X + \cos(300°)Y$$

$$Y' = \frac{\sqrt{3}}{2}X + \frac{1}{2}Y$$

$$C_6^6 = E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(0°)X + \sin(0°)Y$$

$$X' = 1X + 0Y$$

$$Y' = -\sin(0°)X + \cos(0°)Y$$

$$Y' = 0X + 1Y$$

Clockwise [XYZ]

$$C_6^1 = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

$$C_6^1 = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(60°)\, X \sin(60°)Y$$

$$X' = \frac{1}{2}X - \frac{\sqrt{3}}{2}Y$$

$$Y' = \sin(60°)X + \cos(60°)Y$$

$\mathrm{Y'} = -\frac{\sqrt{3}}{2}\mathrm{X} + \frac{1}{2}\mathrm{Y}$

$$\mathrm{C}_6^2 = \mathrm{C}_3^1 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \quad \mathrm{C}_3^1 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$\mathrm{X'} = \cos(120°)\mathrm{X} - \sin(120°)\mathrm{Y}$

$\mathrm{X'} = -\frac{1}{2}\mathrm{X} - \frac{\sqrt{3}}{2}\mathrm{Y}$

$\mathrm{Y'} = \sin(120°)\mathrm{X} + \cos(120°)\mathrm{Y}$

$\mathrm{Y'} = \frac{\sqrt{3}}{2}\mathrm{X} - \frac{1}{2}\mathrm{Y}$

$$\mathrm{C}_6^3 = \mathrm{C}_2^1 = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \quad C_2^1 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$\mathrm{X'} = \cos(180°)\mathrm{X} - \sin(180°)\mathrm{Y}$

$\mathrm{X'} = -1\mathrm{X} - 0\mathrm{Y}$

$\mathrm{Y'} = \sin(180°)\mathrm{X} + \cos(180°)\mathrm{Y}$

$\mathrm{Y'} = 0\mathrm{X} - 1\mathrm{Y}$

$$\mathrm{C}_6^4 = \mathrm{C}_3^2 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \quad \mathrm{C}_3^2 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$\mathrm{X'} = \cos(240°)\mathrm{X} - \sin(240°)\mathrm{Y}$

$\mathrm{X'} = -\frac{1}{2}\mathrm{X} + \frac{\sqrt{3}}{2}\mathrm{Y}$

$\mathrm{Y'} = \sin(240°)\mathrm{X} + \cos(240°)\mathrm{Y}$

$\mathrm{Y'} = -\frac{\sqrt{3}}{2}\mathrm{X} - \frac{1}{2}\mathrm{Y}$

$$\mathrm{C}_6^5 = \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & \frac{1}{2} \end{bmatrix} \quad \mathrm{C}_3^2 = \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$\mathrm{X'} = \cos(300°)\mathrm{X} - \sin(300°)\mathrm{Y}$

$\mathrm{X'} = \frac{1}{2}\mathrm{X} + \frac{\sqrt{3}}{2}\mathrm{Y}$

$\mathrm{Y'} = \sin(300°)\mathrm{X} + \cos(300°)\mathrm{Y}$

$\mathrm{Y'} = \frac{\sqrt{3}}{2}\mathrm{X} + \frac{1}{2}\mathrm{Y}$

$$C_6^6 = E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \quad E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$X' = \cos(0°)X + \sin(0°)Y$$

$$X' = 1X + 0Y$$

$$Y' = -\sin(0°)X + \cos(0°)Y$$

$$Y' = 0X + 1Y$$

Reflections

$$\sigma_{v(XZ)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Eg. Through two points and center

CHAPTER FOUR: OTHER COMMON CHEMICAL GROUP THEORY TEXTBOOK INCONSISTENCIES

4.1 Deriving the C_{3v} character table

The inconsistency of rotation matrix choice can go unnoticed in chemical group theory because the operations are grouped into classes. Two symmetry elements, say A and B, are in the same class if there is an element X within the group where: $X^{-1}AX = B$. The process of surrounding a symmetry element with another element and its inverse is called a similarity transform. The character table for C_{3v} will be derived to show both where a character table comes from and why the choice of clockwise and anticlockwise rotation does not matter once a character table is being used. All four rotation matrices are shown to establish this point.

First the inverse of each operation will be found to obtain X^{-1}.

Mirror planes are their own inverse:

$$\sigma_v = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v{}^{-1} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_v = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v{}^{-1} = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_v = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v{}^{-1} = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Anticlockwise [X Y Z]

$$[X'Y'Z'] = [X\,Y\,Z]\begin{bmatrix}\cos\theta & -\sin\theta & 0\\ \sin\theta & \cos\theta & 0\\ 0 & 0 & 1\end{bmatrix}$$

$$C_3^1 = \begin{bmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix} \quad C_3^2 = \begin{bmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix}$$

C_3^1 and C_3^2 are the inverses of each other:

$$C_3^{1\,-1} = \begin{bmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix}^{-1} = \begin{bmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix} \quad C_3^{2\,-1} = \begin{bmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix}^{-1} = \begin{bmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix}$$

This can also be shown by multiplying them:

$$C_3^2C_3^1 = \begin{bmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix}\begin{bmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix} = \begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix} \quad C_3^1C_3^2 = \begin{bmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix}\begin{bmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix} = \begin{bmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & 1\end{bmatrix}$$

Note the convention is for operations to be carried out from right to left, so $C_3^2C_3^1$ means C_3^1 first and then C_3^2 second.

Clockwise [X Y Z]

$$[X'Y'Z'] = [X\,Y\,Z]\begin{bmatrix}\cos\theta & \sin\theta & 0\\ -\sin\theta & \cos\theta & 0\\ 0 & 0 & 1\end{bmatrix}$$

$$C_3^1 = \begin{bmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix} \quad C_3^2 = \begin{bmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix}$$

C_3^1 and C_3^2 are the inverses of each other:

$$C_3^{1\,-1} = \begin{bmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix}^{-1} = \begin{bmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix} = C_3^2 \quad C_3^{2\,-1} = \begin{bmatrix}-\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix}^{-1} = \begin{bmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\ 0 & 0 & 1\end{bmatrix} = C_3^1$$

This can also be shown by multiplying them:

$$C_3^2C_3^1 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3^1C_3^2 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Anticlockwise $\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$

$$\begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix}$$

$$C_3^1 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3^2 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

C_3^1 and C_3^2 are the inverses of each other:

$${C_3^1}^{-1} = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}^{-1} = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = C_3^2 \quad {C_3^2}^{-1} = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}^{-1} = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = C_3^1$$

This can also be shown by multiplying them:

$$C_3^2C_3^1 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3^1C_3^2 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Clockwise $\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$

$$\begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix}$$

$$R_{CW} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$C_3^1 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3^2 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

C_3^1 and C_3^2 are the inverses of each other:

$$C_3^{1\,-1} = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}^{-1} = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3^{2\,-1} = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}^{-1} = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

This can also be shown by multiplying them:

$$C_3^2 C_3^1 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3^1 C_3^2 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The chart below can be used as AX.

C3v multiplication table

C_{3v}	**E**	C_3^1	C_3^2	σ_{v1}	σ_{v2}	σ_{v3}
E	E	C_3^1	C_3^2	σ_{v1}	σ_{v2}	σ_{v3}
C_3^1	C_3^1	C_3^2	E	σ_{v3}	σ_{v1}	σ_{v2}
C_3^2	C_3^2	E	C_3^1	σ_{v2}	σ_{v3}	σ_{v1}
σ_{v1}	σ_{v1}	σ_{v2}	σ_{v3}	E	C_3^1	C_3^2
σ_{v2}	σ_{v2}	σ_{v3}	σ_{v1}	C_3^2	E	C_3^1
σ_{v3}	σ_{v3}	σ_{v1}	σ_{v2}	C_3^1	C_3^2	E

Order is first the operation at the top of table then the operation on the side

The product from the C_{3v} multiplication table is then multiplied by the inverses calculated above.

$EC_3^1E = C_3^1$

$C_3^2C_3^1C_3^1 = C_3^2C_3^2 = C_3^1$

$C_3^1C_3^1C_3^2 = C_3^1E = C_3^1$

$\sigma_{v1}C_3^1\sigma_{v1} = \sigma_{v1}\sigma_{v3} = C_3^2$

$\sigma_{v2}C_3^1\sigma_{v2} = \sigma_{v2}\sigma_{v1} = C_3^2$

$\sigma_{v3}C_3^1\sigma_{v3} = \sigma_{v3}\sigma_{v2} = C_3^2$

C_3^1 and C_3^2 are in a class together. This should be seen with the similarity transform of C_3^2 as well:

$E C_3^2 E = C_3^2$

$C_3^2 C_3^2 C_3^1 = C_3^2 E = C_3^2$

$C_3^1 C_3^2 C_3^2 = C_3^1 C_3^1 = C_3^2$

$\sigma_{v1} C_3^2 \sigma_{v1} = \sigma_{v1}\sigma_{v2} = C_3^1$

$\sigma_{v2} C_3^2 \sigma_{v2} = \sigma_{v2}\sigma_{v3} = C_3^1$

$\sigma_{v3} C_3^2 \sigma_{v3} = \sigma_{v3}\sigma_{v1} = C_3^2$

All vertical mirror planes are also in a class together:

$E\sigma_{v1}E = \sigma_{v1}$

$C_3^2 \sigma_{v1} C_3^1 = C_3^2 \sigma_{v2} = \sigma_{v3}$

$C_3^1 \sigma_{v1} C_3^2 = C_3^1 \sigma_{v3} = \sigma_{v2}$

$\sigma_{v1}\sigma_{v1}\sigma_{v1} = \sigma_{v1} E = \sigma_{v1}$

$\sigma_{v2}\sigma_{v1}\sigma_{v2} = \sigma_{v2} C_3^1 = \sigma_{v3}$

$\sigma_{v3}\sigma_{v1}\sigma_{v3} = \sigma_{v3} C_3^2 = \sigma_{v2}$

It is now known that $C_3^1$and C_3^2 are in a class together and that σ_{v1}, σ_{v2}, and σ_{v3} are in a class together. E is in a class of its own as well, as $X^{-1}EX = X^{-1}X = E$. The number of classes (3) will equal the number of irreducible representations, which are the rows of the character table.

C_{3v}	**E**	**$2C_3$**	**$3\sigma_v$**		
(1)					
(2)					
(3)					

The irreducible representations are found from the transformation matrices. First the operations are lined up according to class.

Anticlockwise [X Y Z]

$$C_3^3 = E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3^1 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$C_3^2 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_v = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Clockwise $[XYZ]$

$$C_3^3 = E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_3^1 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$C_3^2 = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_v = \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$\sigma_v = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

The matrices are then block diagonalized. In order to do this, all of the non-diagonal elements must be zeros. (The diagonal only includes top left to bottom right. The opposite diagonal is never used.) One then must draw a square matrix around the non-zero elements in a way that isolates them from the zeros. In the identity matrix, a square 1x1 matrix can be drawn around each of the values of 1. However in the C_3 matrices, a 2x2 and a 1x1 matrix must be drawn, as three 1x1 matrices would not isolate all non-zero elements.

$$C_3^1 = \begin{bmatrix} \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} & \begin{matrix} 0 \\ 0 \end{matrix} \\ \begin{matrix} 0 & \quad 0 \end{matrix} & [1] \end{bmatrix}$$

The diagonals are then added (if applicable), and that is the character for the given position (X, Y, or Z). All elements in a class will have the same block diagonal. In the case of C_3, X and Y are block diagonalized together, so they must be treated together as one irreducible representation, (x,y).

Block diagonalized:

	E	$2C_3$	$3\sigma_v$	
X,Y	2	-1	0	E
Z	1	1	1	A_1

The irreducible representations are named using Mulliken notation.

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	s, z	
E	2	-1	0	(x,y)	

The other elements in a character table are found using advanced group theory rules and need not be derived by the student. These irreducible representations can correspond to a rotational mode (which is a different calculation process), or are listed in the character table to satisfy the rules of a group. This means some irreducible representations are mathematically part of the group, but may not have any application to chemical bonding.

4.2 The B_3 representation

A curious thing can be seen in some character tables, where there is a subscript of 3 (on B_3) labeling some irreducible representations in the D_2 and D_{2h} point groups. The Mulliken notation does not define a subscript of 3. Furthermore, the Mulliken notation defines 1 and 2 as absolutes, which leaves no room for a third option:

- When there is a C_2 axis perpendicular to the principal rotation axis:
  - 1 designates the irreducible representation is symmetric with respect to the $\perp C_2$ axis
  - 2 designates the irreducible representation is asymmetric with respect to the $\perp C_2$ axis
- When there is not a $\perp C_2$ axis:
  - 1 designates the irreducible representation is symmetric with respect to a vertical mirror plane
  - 2 designates the irreducible representation is asymmetric with respect to a vertical mirror plane

Inui et al. (1990) write that the Mulliken notation is abandoned in the case of D_2 and D_{2h} because the X,Y, and Z axes are equivalent, but do not provide historical context for why the irreducible representations are labeled B_1 B_2 and B_3. No other sources were found that mention B_3, nor the point groups it is found within. The character tables are derived below to try to answer this question.

4.2.1 The D_2 point group

The D_2 (e.g. twistane) point group table is made up of the following operations*:

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_{2(Z)} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_{2(Y)} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad C_{2(X)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

*C_2 is the special case where it does not matter anticlockwise or clockwise or $[X\ Y\ Z]$ or $\begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$ matrix orientation.

Block diagonalized:

D_2	**E**	**$C_{2(Z)}$**	**$C_{2(Y)}$**	**$C_{2(X)}$**
(s)	1	1	1	1
Z	1	1	-1	-1
Y	1	-1	1	-1
X	1	-1	-1	1

Note the point group table is for the center of symmetry. If this center is an atom, the X, Y, and Z axes can correspond to the px, py, and pz orbitals, which appear in the second column to the right in the character tables. In practice, the center of symmetry for D_2 and D_{2h} molecules does not usually lie on an atom, so these axes will remain labeled X, Y, and Z (after the Cartesian axes) for this treatment.

According to the Mulliken Notation, each irreducible representation should be named with only an A or a B:

- A indicates the operation is symmetric with respect to the principal rotation axis.
- B indicates the operation is asymmetric with respect to the principal rotation axis.
- There is not a $\perp C_2$ axis, nor is there a σ_v, so subscript 1 and 2 should not be included.
- There is not an inversion center, so subscript g and u are not included.
- There is no σ_h, so ’ and ” are not included.

There are two possible ways to label X,Y, and Z. One, Z can be defined arbitrarily as the principal rotation axis even though in the special case of D_2, it is no difference between it and the other two axes. Alternatively, X, Y, and Z can all be considered the principal rotation axis.

If Z is the principal rotation axis:

In the first case, $C_{2(Z)}$ is arbitrarily the principal rotation axis. Rotation about $C_{2(z)}$ is symmetric for Z, and asymmetric for X and Y. This gives Z an A representation while X and Y get the B representation.

D_2	E	$C_{2(Z)}$	$C_{2(Y)}$	$C_{2(X)}$	
A	1	1	1	1	s
A	1	1	-1	-1	z
B	1	-1	1	-1	y
B	1	-1	-1	1	x

Note that while both symmetric with respect to $C_{2(z)}$, the s and pz orbitals are not the same kind of A representation, and while both asymmetric with respect to $C_{2(z)}$, the px and py orbitals are not the same kind of B representation. This is where the Muliken notation has limits within the D_2 point group. A new type of subscript would be limited to simply giving the chemist a way to distinguish between the two types of A and two types of B representations, as there is no other symmetry element to use as a way to tell them apart; there are only C_2 rotations. Nevertheless, an identifying subscript might be helpful when referring to a particular irreducible representation.

D_2	E	$C_{2(Z)}$	$C_{2(Y)}$	$C_{2(X)}$	
A_α	1	1	1	1	s
A_β	1	1	-1	-1	z
B_α	1	-1	1	-1	y
B_β	1	-1	-1	1	x

If X, Y, and Z are all the principal axis:

In the second case, all C_2 axes are the principal rotation axis at the same time, which leaves the question: does the symmetric or asymmetric representation take precedent? When looking at X as the principal rotation axis, $C_{2(X)}$ is symmetric upon rotation, but $C_{2(Y)}$ and $C_{2(Z)}$ are asymmetric upon rotation about X. A decision must be made between A and B. The representation can be A if $C_{2(X)}$ takes precedent, or B if $C_{2(Y)}$ and $C_{2(Z)}$ take precedent.

If looking at each axis and its accompanying C_2 rotation (Eg. Z and $C_{2(Z)}$), one would assign the irreducible representation as A. $C_{2(Z)}$ is symmetric with respect to Z. Likewise, $C_{2(Y)}$ is symmetric with respect to Y and $C_{2(X)}$ is symmetric with respect to X.

D_2	E	$C_{2(Z)}$	$C_{2(Y)}$	$C_{2(X)}$	
A	1	1	1	1	s
A	1	1	-1	-1	z
A	1	-1	1	-1	y
A	1	-1	-1	1	x

However, if each C_2 axis is examined in terms of the other two C_2 axes, the irreducible representations would be labeled B. For example, $C_{2(Z)}$ is asymmetric with respect to $C_{2(Y)}$ and $C_{2(X)}$.

D_2	E	$C_{2(Z)}$	$C_{2(Y)}$	$C_{2(X)}$	
A	1	1	1	1	s
B	1	1	-1	-1	z
B	1	-1	1	-1	y
B	1	-1	-1	1	x

With the Mulliken notation, it is not possible to distinguish between the three A (or B) irreducible representations, pz, py, and px. This likely led a past chemist to use a subscript 1, 2, and 3. This is, however, not appropriate within Mulliken notation, as there is not a perpendicular C_2 axis, nor is there a vertical mirror plane, and these are associated with the subscript 1 and 2 notation. Subscripts of α, β, and γ would be more appropriate in this case:

D_2	E	$C_{2(Z)}$	$C_{2(Y)}$	$C_{2(X)}$	
A	1	1	1	1	s
A_α	1	1	-1	-1	z
A_β	1	-1	1	-1	y
A_γ	1	-1	-1	1	x

Or

D_2	E	$C_{2(Z)}$	$C_{2(Y)}$	$C_{2(X)}$	
A	1	1	1	1	s
B_α	1	1	-1	-1	z
B_β	1	-1	1	-1	y
B_γ	1	-1	-1	1	x

4.2.2 The D_{2h} point group

The D_{2h} (e.g. 1,4-dibromobenzene) point group table is made up of the following operations:

$$E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_{2(Z)} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad C_{2(Y)} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad C_{2(X)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad \sigma_{(XY)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \quad \sigma_{(XZ)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_{(YZ)} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Block diagonalized:

D_{2h}	E	$C_{2(Z)}$	$C_{2(Y)}$	$C_{2(X)}$	*i*	$\sigma_{(XY)}$	$\sigma_{(XZ)}$	$\sigma_{(YZ)}$
(s)	1	1	1	1	1	1	1	1
Z	1	1	-1	-1	-1	-1	1	1
Y	1	-1	1	-1	-1	1	-1	1
X	1	-1	-1	1	-1	1	1	-1

The problem of labeling X,Y, and Z arises again. Z can be defined as the principal rotation axis or X,Y, and Z can all be considered as the principal rotation axis at the same time.

Naming with Mulliken Notation:

- A indicates the operation is symmetric with respect to the principal rotation axis.
- B indicates the operation is asymmetric with respect to the principal rotation axis.
- 1 indicates the operation is symmetric with respect to the $\perp C_2$ axis
- 2 indicates the operation is asymmetric with respect to the $\perp C_2$ axis
- g (gerade) indicates the operation is symmetric with respect to the inversion center
- u (ungerade) indicates the operation is asymmetric with respect to the inversion center
- ’ indicates the operation is symmetric with respect to a horizontal symmetry plane, σ_h
- ” indicates the operation is asymmetric with respect to a horizontal symmetry plane, σ_h

If Z is the principal rotation axis:

If Z is the principal C_2 axis, the other two C_2 axes are perpendicular to the principal axis. The 1 and 2 subscript notation would therefore be used according to the perpendicular C_2 axes, rather than the vertical mirror planes ($\sigma_{(XY)}$ is a horizontal mirror plane). Again, there is the problem of precedent. The reducible can be symmetric or asymmetric with respect to the perpendicular C_2 axis, however in the cases of the two B representations, there is one each of a symmetric and asymmetric C_2 operation. A subscript of 1 or 2 cannot be assigned unless either symmetric (1) and one asymmetric (-1) is defined as more important. The vertical mirror planes also pose an additional problem of having conflicting answers to whether the representation is symmetric or asymmetric. Even if Z is the principal rotation axis, the vertical mirror planes that contain Z can have one symmetric and one asymmetric value for the px and py orbitals. The 1 and 2 subscripts could be left out entirely to combat this problem:

D_{2h}	E	$C_{2(Z)}$	$C_{2(Y)}$	$C_{2(X)}$	*i*	$\sigma_{(XY)}$	$\sigma_{(XZ)}$	$\sigma_{(YZ)}$	
A_{1g}'	1	1	1	1	1	1	1	1	s
A_u"	1	1	-1	-1	-1	-1	1	1	z
$B_{u\alpha}$'	1	-1	1	-1	-1	1	-1	1	y
$B_{u\beta}$'	1	-1	-1	1	-1	1	1	-1	x

Only X and Y would need an additional subscript to distinguish them.

If X, Y, and Z are all the principal axis:

If all C_2 axes are equal, they are all the principal rotation axis at the same time. Because of this, all mirror planes are vertical, σ_v, and none of the mirror planes can be the horizontal mirror plane, σ_h. This rules out all Mulliken notation with primes (' and "). The axes are then treated one at a time: When Z is the principal rotation axis, pz is symmetric to $C_{2(Z)}$, giving us an A representation. Likewise, when Y is the principal rotation axis, py is symmetric to $C_{2(Y)}$, and when X is the principal rotation axis, px is symmetric to $C_{2(X)}$.

D_{2h}	E	$C_{2(Z)}$	$C_{2(Y)}$	$C_{2(X)}$	*i*	$\sigma_{(XY)}$	$\sigma_{(XZ)}$	$\sigma_{(YZ)}$	
(s)	1	1	1	1	1	1	1	1	A
Z	1	1	-1	-1	-1	-1	1	1	A
Y	1	-1	1	-1	-1	1	-1	1	A
X	1	-1	-1	1	-1	1	1	-1	A

There is also the possibility of defining the px, py, and pz irreducible representations as B representations. To do this, the asymmetric operations must take president over the symmetric representation. So while $C_{2(Z)}$ is symmetric with respect to rotation about Z, $C_{2(X)}$ and $C_{2(Y)}$ are asymmetric. As X, Y, and Z are all the principal rotation axis, the irreducible representation could be called asymmetric with respect to the principal rotation axis (that is, to two of the three principal rotation axes).

D_{2h}	E	$C_{2(Z)}$	$C_{2(Y)}$	$C_{2(X)}$	*i*	$\sigma_{(XY)}$	$\sigma_{(XZ)}$	$\sigma_{(YZ)}$	
(s)	1	1	1	1	1	1	1	1	A
Z	1	1	-1	-1	-1	-1	1	1	B
Y	1	-1	1	-1	-1	1	-1	1	B
X	1	-1	-1	1	-1	1	1	-1	B

If all axes are the principal axis, there isn't a perpendicular C_2 axis to use to define the 1 or 2 subscript (the perpendicular C_2 is a different principal rotation axis). At the same time that each axis is the principal rotation axis, it is symmetric with respect to a vertical plane of symmetry. That is, when we look at Z as the principal axis, the pz irreducible representation is symmetric with respect to the mirror planes that contain Z ($\sigma_{(XZ)}$ and $\sigma_{(YZ)}$). This gives the pz, py, and px irreducible representations a subscript of 1.

The last part of the notation is simpler. The pz, py, and px irreducible representations are asymmetric with respect to the inversion center, and get a subscript of u.

D_{2h}	E	$C_{2(Z)}$	$C_{2(Y)}$	$C_{2(X)}$	*i*	$\sigma_{(XY)}$	$\sigma_{(XZ)}$	$\sigma_{(YZ)}$	
s	1	1	1	1	1	1	1	1	A_{1g}
z	1	1	-1	-1	-1	-1	1	1	A_{1u}
y	1	-1	1	-1	-1	1	-1	1	A_{1u}
x	1	-1	-1	1	-1	1	1	-1	A_{1u}

The problem distinguishing between pz, py, and px arises again. The notation of α, β, and γ can be used again:

D_{2h}	E	$C_{2(Z)}$	$C_{2(Y)}$	$C_{2(X)}$	*i*	$\sigma_{(XY)}$	$\sigma_{(XZ)}$	$\sigma_{(YZ)}$	
A_{1g}	1	1	1	1	1	1	1	1	s
$A_{1u\alpha}$	1	1	-1	-1	-1	-1	1	1	z
$A_{1u\beta}$	1	-1	1	-1	-1	1	-1	1	y
$A_{1u\gamma}$	1	-1	-1	1	-1	1	1	-1	x

Note also that the perfectly symmetric representation, A_{1g}, is not always shown with a subscript 1. It should be, however, as it is also symmetric to all vertical mirror planes.

4.2.3 Three B representations

All character tables that were examined showed the irreducible representations that are associated with pz, py, and px labeled as B representations (B_1, B_2, B_3, respectively). Defining Z as the principal rotation axis will get one A and two B irreducible representations. Defining X, Y, and Z equally as the principal rotation axis, will give three A irreducible representations or three B reducible representations.

The only way to derive three B irreducible representations is to define X, Y, and Z each as the principal C_2 rotation axis. If all axes are the principal rotation axis, the irreducible representations (that correspond to X, Y, and Z) will each have one C_2 operation that is symmetric, and two that are asymmetric. For example, the Z axis irreducible representation will show that $C_{2(Z)}$ is symmetric and $C_{2(X)}$ and $C_{2(Y)}$ are asymmetric with respect to rotation about the Z axis. One then has to make the decision that asymmetric operations overrule symmetric operations to give B instead of A designations.

D_2	E	$C_{2(Z)}$	$C_{2(Y)}$	$C_{2(X)}$	
A	1	1	1	1	s
B_α	1	1	-1	-1	z
B_β	1	-1	1	-1	y
B_γ	1	-1	-1	1	x

D_{2h}	E	$C_{2(Z)}$	$C_{2(Y)}$	$C_{2(X)}$	*i*	$\sigma_{(XY)}$	$\sigma_{(XZ)}$	$\sigma_{(YZ)}$	
A_{1g}	1	1	1	1	1	1	1	1	s
$B_{1u\alpha}$	1	1	-1	-1	-1	-1	1	1	z
$B_{1u\beta}$	1	-1	1	-1	-1	1	-1	1	y
$B_{1u\gamma}$	1	-1	-1	1	-1	1	1	-1	x

Under these conditions, three B representations can be derived. There is, however, no reason to have a B_3 representation. The three B representations can be distinguished with the use of an α, β, γ subscript system.

4.2.4 Concluding remarks

There is no precedent for defining the asymmetric representation as more important than the symmetric representation, or the opposite. It is the opinion of the author that the definition should take advantage of the single unique character in each representation. For the D_2 and

D_{2h} point groups (where X,Y, and Z are all defined as the principal rotation axis), this would be the following in bold:

D_2	**E**	**$C_{2(Z)}$**	**$C_{2(Y)}$**	**$C_{2(X)}$**	
A	1	1	1	1	s
A_α	1	**1**	-1	-1	z
A_β	1	-1	**1**	-1	y
A_γ	1	-1	-1	**1**	x

D_{2h}	**E**	**$C_{2(Z)}$**	**$C_{2(Y)}$**	**$C_{2(X)}$**	***i***	**$\sigma_{(XY)}$**	**$\sigma_{(XZ)}$**	**$\sigma_{(YZ)}$**	
A_{1g}	1	1	1	1	1	1	1	1	s
$A_{1u\alpha}$	1	**1**	-1	-1	-1	-1	1	1	z
$A_{1u\beta}$	1	-1	**1**	-1	-1	1	-1	1	y
$A_{1u\gamma}$	1	-1	-1	**1**	-1	1	1	-1	x

If this unique character forms the basis of the definition, an A designation is more appropriate. For example, when Z is the principal rotation axis, the $C_{2(Z)}$ rotation is symmetric (1), and $C_{2(Y)}$ and $C_{2(X)}$ are asymmetric (-1) with respect to the principal rotation axis. Likewise, when Y is the principal rotation axis, $C_{2(Y)}$ is symmetric, and when X is the principal rotation axis, $C_{2(X)}$ is symmetric. Choosing the single symmetric (1) character as more important than the two asymmetric (-1) characters leads to an A representation.

4.3 Propagation of error throughout sources

This section contains an example of the inconsistencies described in Chapter One concerning an author's choice of principal rotation direction and the direction of rotation depicted in the accompanying diagram. In the Principles section of his book, *Chemical Applications of Group Theory, 3rd Ed.*, F. Albert Cotton (1990) derives the transformation matrix for a proper rotation. The Z axis is chosen as the principal rotation axis, but the direction of rotation is not defined. Instead, Cotton lists out the transformation matrices for both clockwise and anticlockwise rotation. The diagram shows an anticlockwise rotation, and Cotton claims to derive the anticlockwise rotation matrix first, however the clockwise rotation matrix is provided instead. From Cotton (1990):

> Suppose that we have a point in the *xy* plane with coordinates x_1 and y_1, as shown in the diagram. This point defines a vector, r_1, between itself and the origin. Now suppose that this vector is rotated through an angle θ so that a new vector, r_2, is produced with a terminus at the point x_2 and y_2. We now inquire about how the final coordinates, x_2 and y_2, are related to the original coordinates, x_1 and y_1, and the angle θ. The relationship is not difficult to work out. When the x component of r_1, x_1, is rotated by θ, it becomes a vector x' which has an x component of x1 cos θ and a y component of $x_1 \sin \theta$. Similarly, the y component of r_1, y_1, upon rotation by θ becomes a new vector y', which has an x component of –y sin θ and a y component of $y_1 \cos \theta$. Now, x_2 and y_2, the components of r_2, must be equal to the sums of the x and y components of x' and y', so we write
>
> $$x_2 = x_1 \cos\theta - y_1 \sin\theta$$
> $$y_2 = x_1 \sin\theta + y_1 \cos\theta$$
>
> The transformation expressed by 4.1-1 can be written in matrix notation in the following way:
>
> $$\begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \end{bmatrix}$$
>
> This result is for a counterclockwise rotation. Because $\cos\phi = \cos(-\phi)$ while $\sin\phi = -\sin(-\phi)$, the matrix for a clockwise rotation through the angle ϕ must be
>
> $$\begin{bmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{bmatrix}$$
>
> Thus, finally, the total mtrix equation for a clockwise rotation through ϕ about the z axis is
>
> $$\begin{bmatrix} \cos\phi & \sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix}$$

In his book, Cotton prefers the vertical transformation matrix. The correct transformation matrices for proper rotation were derived in Chapter Two of this thesis and are:

Anticlockwise

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

Clockwise

$$\begin{bmatrix} X' \\ Y' \\ Z' \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix}$$

From the above excerpt from Cotton (1990):

Cotton's "Counterclockwise"

$$\begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

Cotton's "Clockwise"

$$\begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} \cos\phi & \sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix}$$

What Cotton lists as the anticlockwise rotation matrix is actually the clockwise rotation matrix. Likewise, what is called the clockwise rotation matrix is the clockwise rotation matrix. This error propagates into his next section on improper rotation where the following matrix is given as a clockwise improper rotation when it is an anticlockwise matrix:

$$\begin{bmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

An error such as the one discussed above can create inconsistencies in other publications. This is seen in the *Inorganic Chemistry, 4th Ed.* textbook by Miessler and Tarr (2010). Miessler and Tarr define rotation as anticlockwise early in their molecular symmetry chapter, but later provide a vertical clockwise rotation matrix. An accompanying footnote in the section instructs the student to read more on the subject from Cotton (1990). It is likely that Miessler and Tarr were intending to reference the anticlockwise rotation matrix, but inadvertently used the clockwise matrix that Cotton erroneously labeled anticlockwise.

CHAPTER FOUR REFERENCES

Cotton, F.A. *Chemical Applications of Group Theory*, 3rd Ed.; John Wiley and Sons, Inc.: New York, **1990**. ISBN 0471510949.

Inui, T., Tanabe, Y., Onodera, Y. *Group Theory and Its Applications in Physics*; Springer-Verlag: New York, **1990**. ISBN 3540604457.

Miessler, G.L. and Tarr, D.A. *Inorganic Chemistry*, 4th Ed.; Pearson Prentice Hall: New York, **2010**. ISBN 0136153836.