operations

4.9 Representation of Groups

Any symmetry operation about a symmetry element in a molecule involves the transformation of a set of coordinate x, y and z of an atom into a set of new coordinates x′, y′ and z′. The two sets of coordinates of the atom can be related by a set of equations. This set of equations may also be formulated in matrix notation. Thus each symmetry operation can be represented by a specific matrix. A knowledge of the matrices of the various operations in a molecule will be useful to solve structural problems in chemistry.

This chapter will begin with an account of matrix essential to an understanding the discussion of representation of groups.

A matrix is a rectangular array of numbers or symbol for numbers.

$$\begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix} \text{ or } \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix}$$

Any element of the matrix can be represented by a_{ij}, where i denotes the rows (horizontal set) and j denote the columns (vertical sets). The order or dimension of a matrix is defined by the number of rows and columns. When the number of rows equal the number of columns, the matrix is called as square matrix. The elements a_{ij} of a square matrix for which $i = j$ (i.e., a_{11}, a_{22}, a_{33} etc) are called the diagonal elements, and the other elements are called off–diagonals, when all of the off–diagonal elements of a matrix are zero, the matrix is called as diagonal matrix. The sum of the diagonal elements of a square matrix is called the trace or character of the matrix and is represented by symbol χ(chi).

Diagonal matrix $\begin{bmatrix} 3 & 0 & 0 \\ 0 & 4 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ character of this matrix is 8.

Unit matrix $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ character of this matrix is 3.

Matrices may be added, subtracted, multiplied or divided by using the appropriate rules of matrix algebra. In order to add subtract two matrices, both matrices must be of the same dimension, i.e., same no. of rows and columns. For multiplication, column of A must be equal to row of B.

Representation of Groups—Each symmetry operation in a point group can be represented by a number or more generally, by a matrix of number. The matrices for the different symmetry operation can be obtained by considering the effect of there operations on the components of a two–dimensional vector. The results can then be entended to three dimensions.

Matrix for the identity operation (E)—By identity operation, the components x, y and z of a vector remain unchanged. The equations which represent the effect of identity operation on the vector r are given as :

$$E.x = 1.x + 0.y + 0.z$$

$$E.y = 0.x + 1.y + 0.z$$

$$E.z = 0.x + 0.y + 1.z$$

In matrix form these equations become

$$E\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \times \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Hence matrix for identity operation E is :

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

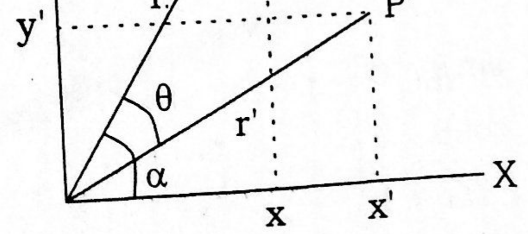
Matrix for rotation operations—The z coordinate will be unchanged by any tion about the z–axis. Thus, the matrix we seek must be in part,

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

The finding the four missing elements can then be solved as a two–nensional problem in the xy plane.

Consider the vector r in the two–dimensional coordinate system as given low. The vector r can be expressed as a column matrix r.

$$r = \begin{bmatrix} x \\ y \end{bmatrix}$$



x and *y* are the components of the vector *r*. The vector *r* be rotated clockwise through an angle θ such that the components of the vector becomes *x*′ and *y*. The resulting vector *r*′.

$$r' = \begin{bmatrix} x' \\ y \end{bmatrix} = C_n . r$$

$$x' = r\cos(\alpha - \theta)$$

$$= r(\cos\alpha . \cos\theta + \sin\alpha . \sin\theta)$$

$$= r\cos\alpha . \cos\theta + r\sin\alpha . \sin\theta$$

$$x' = x\cos\theta + y\sin\theta \qquad \dots \text{(i)}$$

and

$$y' = r\sin(\alpha - \theta)$$

$$= r\sin\alpha . \cos\theta - r\cos\alpha . \sin\theta$$

$$= y\cos\theta - x\sin\theta$$

$$y' = y\cos\theta - x\sin\theta \qquad \dots \text{(ii)}$$

These equations (i) & (ii) are represented in the matrix form as follows :

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \times \begin{bmatrix} x \\ y \end{bmatrix}$$

This eq^n. is just like

$$r' = C_n . r$$

$$\therefore \; C_n = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$$

C_n represents the matrix for rotation operation. In three dimension the matrix $C_n(z)$ become

$$C_n(z) = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Matrix for reflection operation :

Consider the vector *r* with the components *x* and *y*. By reflection across the yz plane, the components x and y becomes *x'* and *y'*. *x'* and *y'* are related as

$$x' = -1x + 0y$$

$$y' = 0x + 1y$$

Matrix for this is

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} \times \begin{bmatrix} x \\ y \end{bmatrix}$$

The reflection operation σ_{yz} is expressed as

$$r' = \sigma_{yz}$$

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

In three dimension

$$\sigma_{y2} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \sigma_{xy} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Like this $\sigma_{x_z} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

Matrix for inversion operation (*i*) :

The *x*, *y* and *z* component of a vector *r* are transformed into their respective negative by the inversion operation.

$$i.x = -1x + 0y + 0z$$

$$i.y = 0x - 1y + 0z$$

$$i.z = 0x + 0y \times 0z$$

$$\therefore\ i \times \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \times \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

The matrix for inversion operation is

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

Matrix for improper rotation (S_n) :

Improper rotational axis will be obtained by rotation axis multiplied by σ_n

$$S_n = C_n,\ \sigma_{xy}(\sigma_h)$$

Matrix of $C_n X$ matrix of σ_{xy}

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

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

The character of the matrices corresponding to the symmetry operations are as follows :

Symmetry operation	**Character of the matrix**
Identity (E)	3
Proper rotation (C_n)	$2\cos\theta + 1$
Reflection (σ)	1
Inversion (i)	–3
Improper rotation (S_n)	$2\cos\theta - 1$