UTILITY OF MATRIX REPRESENTATION IN GROUP THEORY

INTRODUCTION

Symmetry properties of molecules play an important role in analyzing their physical and chemical features. The matrix representation of symmetry operations and point groups are quite useful tools for the purpose.

There are an infinite number of ways of choosing matrices to represent symmetry operations. The choice of representation is determined by its basis i.e. by the labels or functions attached to the objects. A convenient basis to use is by considering the effect of symmetry operations on a 3-D vector whose components are x,y,z. Column matrices are used to represent vectors, which are characterized by their lengths and directions. A special square matrix called unit matrix (containing equal number of rows and columns) is used to represent symmetry operations which help to solve structural problems in chemistry.

In this paper the matrices of various symmetry operations/elements and their applications in representation of point groups have been explained.

WHAT IS A MATRIX?

A matrix is a rectangular array of numbers written down in rows and columns. This entire array is enclosed in square brackets. There are various types of matrices which include Rectangular matrix, Column matrix, Row matrix, Zero matrix, Square matrix, Diagonal matrix, Unit matrix etc. Of all the matrices, there are some special types of matrices (mainly Unit matrix and Column matrix) which are useful in Group Theory.

MATRIX REPRESENTATION OF SYMMETRY OPERATIONS

All symmetry operations can be represented by matrices. These matrices are known as transformation matrices or matrix representation of symmetry operations. We can derive the transformation matrices of different symmetry operations taking into consideration the effect of the symmetry operations on a three dimensional vector whose components are (x,y,z) i.e. a point whose coordinates are (x,y,z).

The transformation matrices of symmetry operations are explained as under:

(i) **Transformation Matrix for Identity Element (E) or E-matrix**

The identity operation is a “doing-nothing” operation that leaves all the three components of a vector (x,y,z) unchanged. This may be written as:

$$E\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

OR

Ex = 1x +0y+0z
Ey =0x+1y +0z
Ez = 0x +0y +1z

The matrix form of these equations is :

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

The matrix of coefficients is a unit matrix in the case. Therefore, E-matrix has the form:

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

(ii) **Transformation Matrix for Mirror Plane (σ) $or\ \sigma -$ Matrix :**

For the purpose of working out transformation matrix for mirror plane, the reflection plane is chosen to lie along with one of the principle Cartesian plane i.e. xy, yz or zx or that planes are now designated as σxy, $\sigma yz, \sigma zx$.

e.g. - The mirror plane σ xy transforms the components of the vector (x,y,z) into (x,y,-z)

$$\sigma xy \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ y \\ -z \end{bmatrix}$$

OR

σ_{xy}x=1x+0y+0z

σ_{xy}y =0x+1y+0z

σ_{xy}z =0x+0y-1z

The matrix form of these equations is-

$$\sigma xy \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

Thus σ-matrix has the form

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

By analogy

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

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

(iii) **Transformation Matrix for the Inversion Centre (i) or i -Matrix :**

In this operation, every atom in the molecule is moved in a straight line through inversion centre to the opposite side of the molecule.

The inversion centre(i) transforms the components of the vector(x,y,z)into (-x,-y,-z)

This may be written as-

$$i \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ -z \end{bmatrix}$$

Or

ix=-1x+0y+0z

iy=0x-1y+0z

iz=0x+0y-1z

The matrix form of equations is –

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

Hence i-matrix gets the form as:

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

(iv) **Transformation Matrix for the Proper Rotation Axis or C_{n-} Matrix**

The dimension of proper rotation axis C_n is 1. Hence, one of the coordinates will remain unchanged and other coordinates will change sign. The coordinate which does not change its sign is the coordinate about which the rotation is affected.

Let us consider C_n rotation about z-axis. The components of the vector (x,y,z) become(-x,-y,z). The transformation matrix of proper rotation axis (C_n^z) in anticlockwise direction is given by-

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

e.g. For C_2^z, $\theta = \underline{360^0/2} = 180^0$

Substituting $\theta=180^0$, C_2^zmatrix takes the form= $\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

Hence, any $C_n(z)$ matrix can be deduced by substituting appropriate values of θ.

(v) **Transformation Matrix for the Improper Rotation Axis or S_n- Matrix:**
In this operation, molecule is rotated by n-fold rotation followed by reflection through mirror plane perpendicular to the rotation axis.

If rotational axis C_n is taken as z-axis, then by definition $S_n(z)= C_n(z). \sigma xy$ where $C_n(z)$ and σxy are perpendicular to each other.

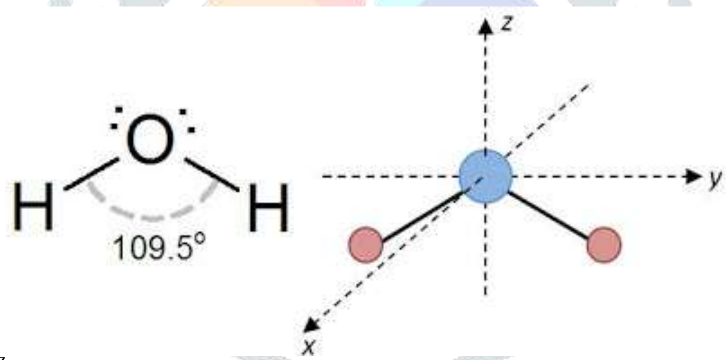
$$S_n(z) = \begin{bmatrix} cos\theta & -sin\theta & 0 \\ sin\theta & cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} = \begin{bmatrix} cos\theta & -sin\theta & 0 \\ sin\theta & cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

Similarly, Sn(x) and Sn(y) matrices can be obtained from corresponding matrices of Cn(x) and Cn(y) by taking their product with σxz and σyz respectively.

MATRIX REPRESENTATION OF POINT GROUPS
Similar to matrices of symmetry operations, the transformation matrices of point groups can be derived in the following manner:

A set of symmetry elements constitute a point group if all the four properties (closure, identity, inverse and associative)are satisfied. The matrices representing each of these elements also should satisfy these rules.

Consider water molecule which belongs to C_2v group-



The 4 elements of this group are E, C_2^Z , σxz and σyz.

The transformation matrices of these elements are

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

E $\quad C_2 \quad \sigma xz \quad \sigma yz$

Like the elements of a point group, the corresponding transformation matrices also satisfy the group properties.

Illustration:

IDENTITY PROPERTY

In any group, there must be one element which commutes with all other elements and leaves them unchanged.

The unit matrix identity $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$ commutes with all the matrices and leaves them unchanged. So it is the transformation matrix of E.

INVERSE PROPERTY

Every element must have an inverse (also known as reciprocal) which is also an element of the group. The inverse is an element such that $A.A^{-1}=E$

$$\underset{\sigma yz}{\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}} \quad \underset{\sigma yz}{\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}} = \underset{E}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}$$

- The matrix of σyz is its own inverse.
- In fact the matrix of every element is its own inverse in the C_{2v} point group.

From the above it is clear that the symmetry operations in a group may be represented by a set of transformation matrices. Each individual matrix is called a representative of the corresponding symmetry operations, and the complete set of matrix is called a matrix representation of the group. The matrix representations act on some chosen basis sets of functions. As the matrices behave very similar to symmetry operations, therefore, theories about matrices can be used for solving chemical problems.

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