Trakia Journal of Sciences, No 4, pp 392-396, 2017

Available online at:
http://www.uni-sz.bg

ISSN 1313-7069 (print)
ISSN 1313-3551 (online) **doi:10.15547/tjs.2017.04.023**

Original Contribution

MATRIX REPRESENTATIONS OF THE COORDINATES OF THE ATOMS OF THE MOLECULES OF H_2O AND NH_3 IN OPERATIONS OF SYMMETRY

M. Ivanova[1]*, L. Dospatliev[2]

[1]Department of Informatics and Mathematics, Trakia University, Stara Zagora, Bulgaria
[2]Department of Pharmacology, Animal Physiology and Physiological Chemistry, Trakia University Stara Zagora, Bulgaria.

ABSTRACT
The molecule is a spatial arrangement of atoms that make it up. This arrangement defines its geometric structure. Knowing the geometry and ways to describe to great advantage in studying the electronic structure of molecules as between geometric and electronic structure there is a close connection.

Key words: operations of symmetry, matrix, H_2O, NH_3

INTRODUCTION

The geometric structure of a molecule is described by the theory of point group symmetry. A fundamental concept in the theory of point groups is of geometric configuration.

Under operation of symmetry along action, which transforms a geometric configuration of a given molecule in another configuration, which is identical or equivalent to the original. From this definition, it follows that in carrying out operation of symmetry equivalent atoms can be swapped or at best remain in place (1-5).

The operations of the symmetry are carried out with respect to the elements of symmetry. The elements of symmetry are geometric concepts - axes, planes, points or combinations thereof. Obviously, not every point, axis and plane that we can spend in space it occupies a molecule is an element of symmetry (3-7).

In **Table 1** are presented the elements, operations of symmetry and symbols which are used for their determination.

Table 1. *Elements and operations of symmetry*

Element	Symbol	Operations	Symbol
Axis	C	Rotation	$\hat{C}$
Plane	σ	Reflection	$\hat{\sigma}$

From the geometry it is known that each point in 3-dimensional space is represented by three coordinates using the orthogonal coordinate system are (x, y, z), in the polar coordinate system are (r, θ, φ) etc. For a description in the space of one molecule of N atom needed $3N$ coordinates
$(x_1, y_1, z_1; x_2, y_2, z_2; \ldots; x_N, y_N, z_N)$.
Let us examine what happens to the coordinates of the atoms in the molecule in carrying out any operation of symmetry of the molecule as a whole, through the following two examples.

- The water molecule

Let us consider the molecule of water as the local coordinates of the atoms in the molecule and the global coordinates of the entire molecule coincide with those in the oxygen atom, as represented in **Figure 1**.

***Correspondence to**: *M. Ivanova, Department of Informatics and Mathematics, Trakia University, Stara Zagora, 6000, Bulgaria; E-mail: mirkaiv@yahoo.com*

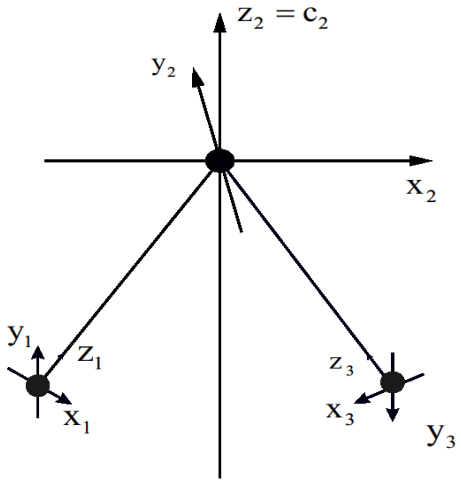

Figure 1. Local coordinates of atoms in a molecule of water and the global coordinates of the entire molecule (coincide with those on the oxygen atom).

C_2 axis is chosen to coincide with the axis of z_2 atoms of oxygen, i.e.

$$H_1 : (x_1, y_1, z_1); \quad O : (x_2, y_2, z_2); \quad H_3 : (x_3, y_3, z_3). \qquad (1)$$

In operation $\hat{C}_2$ atoms H_1 and H_2 swapped places. Then the new coordinates of the atoms resulting from $\hat{C}_2$ are:

$$\begin{aligned} x_1' &= +1.x_3, & x_2' &= -1.x_2, & x_3' &= +1.x_1, \\ y_1' &= +1.y_3, & y_2' &= -1.y_2, & y_3' &= +1.y_1, \\ z_1' &= +1.z_3, & z_2' &= +1.z_2, & z_3' &= +1.z_1. \end{aligned} \qquad (2)$$

This is a little unusual and extravagant way of recording, since we put the +1 and -1 instead of just characters in respective equations. Obviously equations (2) would look differently if we were oriented axes at the respective atoms (local coordinate systems) pointing in different directions. Then the x coordinate of an atom after surgery symmetry would become a mixture of x, y, z in the most general case. The choice of local coordinate systems was designed so as to obtain the simplest possible draws. The orientation of the coordinate axes in space is irrelevant and therefore it is best to choose the most convenient.

Equations (2) can be written in the following matrix form:

$$\begin{bmatrix} x_1' \\ y_1' \\ z_1' \\ x_2' \\ y_2' \\ z_2' \\ x_3' \\ y_3' \\ z_3' \end{bmatrix} = \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{bmatrix} \qquad (3)$$

In (3) the old and new coordinates of the atoms are represented as a matrix column (this is the matrix representation of a vector) right and left of the equality, respectively. A square matrix of numbers -1, 0 and 1 shows how the coordinates are converted into new ones. Therefore, it is called the transformation matrix, in this case - transformation matrix of the coordinates of the atoms of water molecules under the influence of the operation of symmetry $\hat{C}_2$. From (3) to get as coordinate x_1' appropriate corresponding row of square matrix can be multiplied by the column of the coordinates, i.e.

$$x_1' = 0.x_1 + 0.y_1 + 0.z_1 + 0.x_2 + 0.y_2 + 0.z_2 + 1.x_3 + 0.y_3 + 0.z_3 = x_3$$

The equations (2) and (3) are the same, which could easily be convinced if you do the multiplication of the transformation matrix and matrix column in the old coordinates. Conversely, the transformation matrix in (3) was written using the equations (2); we put a +1 or -1 only where need to be replicated equations (2).

The square matrix of type (9 × 9) in (3) is written so that it is clear which group of matrix elements which refers atom. Let us remark that this matrix contains zero elements in that block, which corresponds to an atom, which becomes atom displacements. For example H_1 (the first atom) under the effect of $\hat{C}_2$ becomes H_3 and the third block of the transformation matrix are non-zero elements. Atom 2 remains in place and in the second block on the second row are obtained non-zero matrix elements. In other words, the diagonal of the matrix are obtained non-zero elements only to those atoms which during operation of symmetry remain in place.

For each of the operations of the symmetry of the molecule of water (group C_{2v}, operations $\hat{E}, \hat{C}_2, \hat{\sigma}_1, \hat{\sigma}_2$) we can write transformation matrix similar to that of $\hat{C}_2$ in (3). A total of four operations molecule of water will get four transformation matrices of type (9×9). Even for such a small molecule such as that of water four matrices are large. For each molecule of N atoms transformation matrices have dimensions $(3N\times 3N)$.

Let us now from the water molecule to consider only the three axes (coordinate functions) x, y, z of the atom of oxygen, which is the fixed point in all operations of symmetry for the molecule consideration. Then (3) passes in

$$\begin{pmatrix} x_2' \\ y_2' \\ z_2' \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix},$$

which we can write as

$$\begin{pmatrix} x_2' \\ y_2' \\ z_2' \end{pmatrix} = \hat{C}_2 \qquad \begin{pmatrix} x_2' \\ y_2' \\ z_2' \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x_2 \\ y_2 \\ z_2 \end{pmatrix},$$

which expresses the fact that the new functions are obtained by the action of $\hat{C}_2$ on old functions like the action is represented by the matrix

$$\hat{C}_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad (4)$$

We obtained the transformation matrix of the three coordinates of the atom of oxygen under the action of the operation $\hat{C}_2$. Similarly for the other three operations of symmetry, we get

$$\hat{E} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \hat{\sigma}_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad \hat{\sigma}_2 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \qquad (5)$$

Since oxygen atom stays in place and the four operations of its symmetry axes remain the same as or maintaining orientation (come matrix element $+1$) or routed (matrix element -1), but not translated into coordinates other atoms.

The advantages offered by the recording of the operations of symmetry by means of transformation matrices are large. Rather than track what happens to individual atoms when performing an operation of symmetry we can do the same with matrices of these operations. For example, the product $\hat{\sigma}_1 \otimes \hat{\sigma}_2$ we could find by multiplying matrices $\hat{\sigma}_1$ and $\hat{\sigma}_2$, namely:

$$\underbrace{\begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{\hat{\sigma}_1} \otimes \underbrace{\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{\hat{\sigma}_2} = \underbrace{\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}}_{\hat{C}_2}.$$

The result is a transformation matrix of operation $\hat{C}_2$.

Table 2 shows the result of multiplication operations of symmetry of a molecule of water.

Table 2. *Table of multiplication operations of symmetry in the molecule of the water*

C_{2v}	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_1$	$\hat{\sigma}_2$
$\hat{E}$	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_1$	$\hat{\sigma}_2$
$\hat{C}_2$	$\hat{C}_2$	$\hat{E}$	$\hat{\sigma}_2$	$\hat{\sigma}_1$
$\hat{\sigma}_1$	$\hat{\sigma}_1$	$\hat{\sigma}_2$	$\hat{E}$	$\hat{C}_2$
$\hat{\sigma}_2$	$\hat{\sigma}_2$	$\hat{\sigma}_1$	$\hat{C}_2$	$\hat{E}$

In general, if the molecule rotates about an axis of symmetry of the angle φ, then the transformation matrix of the three axes of an atom which lies on the axis and which z axis coincides with the axis of symmetry, is:

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \hat{C}(\varphi) \qquad \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} \cos\varphi & -\sin\varphi & 0 \\ \sin\varphi & \cos\varphi & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}.$$

This matrix shows that the values of φ, which is $\sin\varphi$ different from zero, the new x' and y' represent a mixture of old x and y, namely:

$$x' = \cos\varphi.x - \sin\varphi.y + 0.z$$

$$y' = \sin\varphi.x + \cos\varphi.y + 0.z$$

When $\varphi = \frac{2\pi}{3}$ (rotation around C_3), we get

$$x' = \left(-\frac{1}{2}\right)x - \frac{\sqrt{3}}{2}y$$

$$y' = \frac{\sqrt{3}}{2}x + \left(-\frac{1}{2}\right)y.$$

Analogously to the example of the water we can be presented, and an example of an ammonia molecule (NH_3), whose molecule is made up of four atoms.

- The ammonia molecule

The ammonia molecule belongs, in its ground-state equilibrium geometry, to the C_{3v} point group. Its symmetry operations consist of two C_3 rotations, $\hat{C}_3$, $\hat{C}_3^2$ (rotations by $\frac{2\pi}{3}$ and $\frac{4\pi}{3}$, respectively about an axis passing through the nitrogen atom and lying perpendicular to the plane formed by the three hydrogen atoms), three vertical reflections, $\hat{\sigma}_v$, $\hat{\sigma}_v'$, $\hat{\sigma}_v''$, and the identity operation $\hat{E}$. Corresponding to these six operations are symmetry elements: the three-fold rotation axis, C_3 and the three symmetry planes σ_v, σ_v' and σ_v'' that contain the three NH bonds and the z-axis **(Figure 2).**

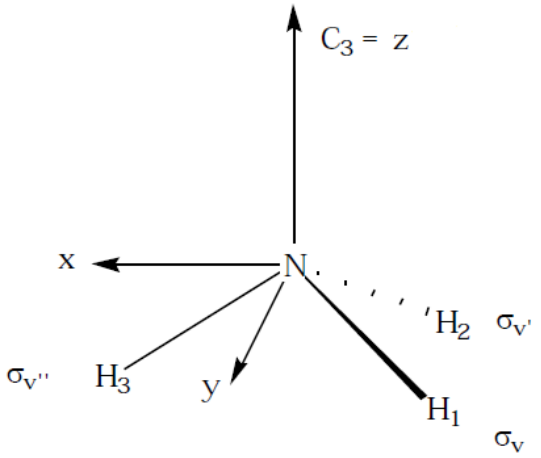

Figure 2. The C_{3v} symmetry group of ammonia

Table 3 shows the result of multiplication operations of the symmetry of the ammonia molecule.

Table 3. *Table multiplication operations of symmetry in the ammonia molecule*

C_{3v}	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{\sigma}_v$	$\hat{\sigma}_v'$	$\hat{\sigma}_v''$
$\hat{E}$	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{\sigma}_v$	$\hat{\sigma}_v'$	$\hat{\sigma}_v''$
$\hat{C}_3$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{E}$	$\hat{\sigma}_v'$	$\hat{\sigma}_v''$	$\hat{\sigma}_v$
$\hat{C}_3^2$	$\hat{C}_3^2$	$\hat{E}$	$\hat{C}_3$	$\hat{\sigma}_v''$	$\hat{\sigma}_v$	$\hat{\sigma}_v'$
$\hat{\sigma}_v$	$\hat{\sigma}_v$	$\hat{\sigma}_v''$	$\hat{\sigma}_v'$	$\hat{E}$	$\hat{C}_3^2$	$\hat{C}_3$
$\hat{\sigma}_v'$	$\hat{\sigma}_v'$	$\hat{\sigma}_v$	$\hat{\sigma}_v''$	$\hat{C}_3$	$\hat{E}$	$\hat{C}_3^2$
$\hat{\sigma}_v''$	$\hat{\sigma}_v''$	$\hat{\sigma}_v'$	$\hat{\sigma}_v$	$\hat{C}_3^2$	$\hat{C}_3$	$\hat{E}$

Note the reflection plane labels do not move. That is, although we start with H_1 in the σ_v plane, H_2 in $\hat{\sigma}_v^{'}$, and H_3 in $\sigma_v^{''}$, if H_1 moves due to the first symmetry operation, σ_v remains fixed and a different H atom lies in the σ_v plane.

Take (x, y, z) as the basic, the matrix of all the operations in C_{3v} group $\left\{\hat{E}, \hat{C}_3, \hat{C}_3^2, \hat{\sigma}_v, \hat{\sigma}_v^{'}, \hat{\sigma}_v^{''}\right\}$ are shown in **Table 4.**

Table 4. *Reducible representations of* C_{3v}

Operations	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{\sigma}_v$	$\hat{\sigma}_v^{'}$	$\hat{\sigma}_v^{''}$
Reducible Representations	$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$

CONCLUSION

A matrix representation of the operations of symmetry helps us understand molecular structure, some chemical properties, and characteristics of physical properties (spectroscopy) – used with group theory to predict vibrational spectra for the identification of molecular shape, and as a tool for understanding electronic structure and bonding.

REFERENCES

1. Wiberg, E., Wiberg, N., Holleman, A. F. *Inorganic Chemistry*. Academic Press, pp 163-164, 2001.
2. Chan, G. K.-L. and Sharma, S., The Density Matrix Renormalization Group in Quantum Chemistry. *Annual review of physical chemistry*, 62: 465 - 481, 2011.
3. Marti, K. H. and Reiher, M., New electron correlation theories for transition metal chemistry. *Physical Chemistry Chemical Physics*, 13: 6750 - 6759, 2011.
4. Legeza, O., Rohwedder, T. and Schneider, R., Numerical Approaches for High-Dimensional PDE's for Quantum Chemistry in Encyclopedia of Applied and Computational Mathematics, B. Engquist, 2012.
5. Chan, G. K.-L., Low entanglement wavefunctions. *Computational Molecular Science*., 2: 907 - 920, 2012.
6. Cotton, F. A., Chemical Applications of Group Theory. Third ed., John Wiley & Sons: Canada 2: 8,1990.
7. Tagliacozzo, L., Evenbly, G. and Vidal, G., Simulation of two-dimensional quantum systems using a tree tensor network that exploits the entropic area law. *Physical Review B.*, 80: 235127 - 235146, 2009.