ELSEVIER

Journal of Molecular Structure (Theochem) 571 (2001) 91–98

THEO CHEM

www.elsevier.com/locate/theochem

A matrix representation for the geometrical algorithm to search the conformational space (GASCOS) for flexible linear molecules

L.N. Santagata[a], F.D. Suvire[b], R.D. Enriz[b,*]

[a]*Departamento de Fisica, Facultad de Fisica, Matematicas y Naturales. Universidad Nacional de San Luis, Chacabuco 917, 5700, San Luis, Argentina*

[b]*Departamento de Quimica, Facultad de Quimica, Bioquimica y Farmacia. Universidad Nacional de San Luis, Chacabuco 917, 5700, San Luis, Argentina*

Received 12 March 2001; accepted 16 April 2001

Abstract

Matrix representation has been developed for two successive rotations (α, β) in order to calculate easily the atomic coordinates (as well as non-bonded distances) from the initial molecular geometry and the dihedral angles applied (α, β). It has been shown that the numerical quantities in the matrices involved, can be calculated from the initial molecular configuration. In addition to these matrices only analytic functions were needed with explicit dependence on the dihedral angles (α, β) to calculate the position vectors of the constituting atoms. Hopefully, the generalized method can be adapted to peptide folding with particular emphasis to the side-chain/side chain interaction.

Keywords: Matrix equations; Geometrical search; Conformational space; Flexible molecules; Molecular folding; Non-bonded distances; Side-chain interaction in proteins

1. Introduction

Previously, we report a systematic search method called Geometrical Algorithm to Search the Conformational Space (GASCOS) for open chain compounds [1]. More recently, we extended the capability of this algorithm for the study of conformationally flexible cyclic molecules [2,3]. It is evident that it is desirable to write, in an explicit form, these equations which are related to the successive rotations of atoms. Such equations should contain numerical quantities obtained from the starting configuration, as well as trigonometric functions which depend, in an explicit way, on the torsional angles applied. It is clear that such expressions, will allow us to determine, in an analytical way, the Cartesian coordinates of all the atoms in a molecule. Thus, we will be able to calculate geometrical quantities (e.g. non-bonded distances) which are function only of the dihedral angles when the bond lengths are fixed. The interatomic distances between non-bonded atoms and, in particular, those distances used as ring closure condition in the cyclic compounds [2,3], can illustrate this point very well. It must be pointed out however, that due to the mathematical complexity of these equations, we need to use a rather compact notation. Thus, the use of well-defined matrices might be the best choice for this purpose.

We wish to report here a matrix notation for those equations obtained for linear molecules and used in developing the GASCOS algorithm [1]. In the first step, we introduce this notation using only the rotation of one atom and subsequently we extend it for the case of two atoms in successive rotations.

* Corresponding author. Fax: +54-2652-4311301.
E-mail address: denriz@unsl.edu.ar (R.D. Enriz).

0166-1280/01/$ - see front matter
PII: S0166-1280(01)00571-1

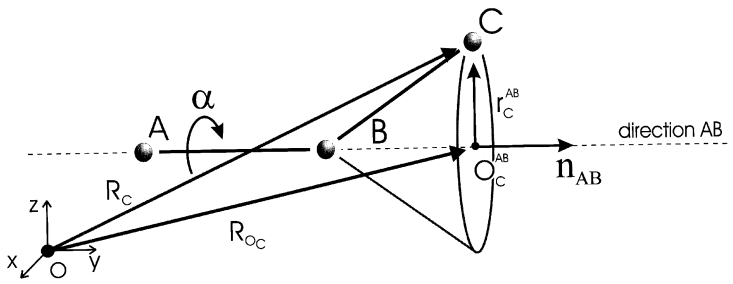

Fig. 1. Vector model for a single rotation by α about the direction of the AB bond, characterized by the unit vector $\mathbf{n}_{AB}$. Note that the position vector for atom C ($\mathbf{R}_C$) is with respect to the arbitrary selected origin (O). All other symbols are defined in the text.

2. Results and discussion

2.1. Definitions and matrix notation for a single rotation

Let us assume that an atom, denoted by C, is rotating about the AB direction, determined by atoms A and B, like shown in Fig. 1. The radius vector $\mathbf{r}_C^{AB}$ indicate the revolution radius of atom C, which is performing a circular trajectory, with respect to O_C^{AB} center.

Previously [1] we reported an expression to calculate the position vector of an atom under such rotation by α. Considering $\mathbf{R}_C^i$ to be the initial position vector of atom C and $\mathbf{R}_C(\alpha)$ its position vector after the rotation by α, we had

$$\mathbf{R}_C(\alpha) = \mathbf{R}_C^i + (\mathbf{n}_{AB} \times \mathbf{r}_C^{i,AB})\sin\alpha + \mathbf{r}_C^{i,AB}(\cos\alpha - 1) \tag{1}$$

where $\mathbf{n}_{AB}$ is the unit vector determining the direction of the AB rotation (see Fig. 1) and $\mathbf{r}_C^{i,AB}$ is the initial revolution radial vector (before it is rotated by α).

From the cross product $\mathbf{n}_{AB} \times \mathbf{r}_C^i$, incorporated in Eq. (1), each component of $\mathbf{R}_C(\alpha)$ might be written as Eq. (2):

$$\begin{aligned}
x_C^{AB} &= x_C^{i,AB} + (\cos\alpha - 1)r_{Cx}^{i,AB} - (n_{AB})_x r_{Cy}^{i,AB}\sin\alpha \\
&\quad + (n_{AB})_y r_{Cz}^{i,AB}\sin\alpha \\
y_C^{AB} &= y_C^{i,AB} + (n_{AB})_z r_{Cx}^{i,AB}\sin\alpha + (\cos\alpha - 1)r_{Cy}^{i,AB} \\
&\quad - (n_{AB})_x r_{Cz}^{i,AB}\sin\alpha \\
z_C^{AB} &= z_C^{i,AB} - (n_{AB})_y r_{Cx}^{i,AB}\sin\alpha + (n_{AB})_x r_{Cy}^{i,AB}\sin\alpha \\
&\quad + (\cos\alpha - 1)r_{Cz}^{i,AB}
\end{aligned} \tag{2}$$

where $(x_C^{i,AB}, y_C^{i,AB}, z_C^{i,AB})$ are the initial coordinates of atom C, and $[(n_{AB})_x, (n_{AB})_y, (n_{AB})_z]$ are the components of the unit vector $\mathbf{n}_{AB}$. Furthermore $(r_{Cx}^{i,AB}, r_{Cy}^{i,AB}, r_{Cz}^{i,AB})$ are the initial components for the revolution radius vector $\mathbf{r}_C^{AB}$.

Defining following column vectors[1] Eq. (3)

$$\underline{\mathbf{R}}_C = \begin{pmatrix} x_C^{AB} \\ y_C^{AB} \\ z_C^{AB} \end{pmatrix} \quad \underline{\mathbf{R}}_C^i = \begin{pmatrix} x_C^{i,B} \\ y_C^{i,AB} \\ z_C^{i,AB} \end{pmatrix} \quad \underline{\mathbf{r}}_C^{i,AB} = \begin{pmatrix} r_{Cx}^{i,AB} \\ r_{Cy}^{i,AB} \\ r_{Cz}^{i,AB} \end{pmatrix} \tag{3}$$

it is possible to write Eq. (2) as Eq. (4)

$$\begin{pmatrix} x_C^{AB} \\ y_C^{AB} \\ z_C^{AB} \end{pmatrix} = \begin{pmatrix} x_C^{i,AB} \\ y_C^{i,AB} \\ z_C^{i,AB} \end{pmatrix} + \begin{pmatrix} \cos\alpha - 1 & -n_z^{AB}\sin\alpha & n_y^{AB}\sin\alpha \\ n_z^{AB}\sin\alpha & \cos\alpha - 1 & -n_x^{AB}\sin\alpha \\ -n_y^{AB}\sin\alpha & n_x^{AB}\sin\alpha & \cos\alpha - 1 \end{pmatrix} \begin{pmatrix} r_{Cx}^{i,AB} \\ r_{Cy}^{i,AB} \\ r_{Cz}^{i,AB} \end{pmatrix} \tag{4}$$

In turn, the detailed Eq. (4) might be expressed in a matrix short-hand form as Eq. (5)

$$\underline{\mathbf{R}}_C = \underline{\mathbf{R}}_C^i + \underline{\underline{\mathbf{M}}}_{AB}(\alpha)\underline{\mathbf{r}}_C^{i,AB} \tag{5}$$

where the square matrix $\underline{\underline{\mathbf{M}}}_{AB}(\alpha)$, used in Eq. (5), is

[1] We represents a square matrix **A** by the symbol $\underline{\underline{\mathbf{A}}}$ and a column vector **B** (or b) by the symbol $\underline{\mathbf{B}}$ (or $\underline{\mathbf{b}}$).

defined as in Eq. (6)

$$\underline{\underline{\mathbf{M}}}_{AB}(\alpha) = \begin{pmatrix} \cos\alpha - 1 & -n_z^{AB}\sin\alpha & n_y^{AB}\sin\alpha \\ n_z^{AB}\sin\alpha & \cos\alpha - 1 & -n_x^{AB}\sin\alpha \\ -n_y^{AB}\sin\alpha & n_x^{AB}\sin\alpha & \cos\alpha - 1 \end{pmatrix} \tag{6}$$

It should be noted that the $\underline{\underline{\mathbf{M}}}_{AB}(\alpha)$ matrix Eq. (6) has in all its diagonal elements $(\cos\alpha - 1)$ and in its off-diagonal elements are possessing $\sin\alpha$. Therefore, it is possible to rewrite Eq. (6) as the addition of two matrices as shown in Eq. (7)

$$\underline{\underline{\mathbf{M}}}_{AB}(\alpha) = (\cos\alpha - 1)\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + \sin\alpha\begin{pmatrix} 0 & -n_z & n_y \\ n_z & 0 & -n_x \\ -n_y & n_x & 0 \end{pmatrix} \tag{7}$$

Thus, utilizing Eq. (7), Eq. (6) may be simplified as shown in Eq. (8)

$$\underline{\underline{\mathbf{M}}}_{AB}(\alpha) = (\cos\alpha - 1)\underline{\underline{\boldsymbol{M}}} + (\sin\alpha)\underline{\underline{\mathbf{1}}}(\mathbf{n}_{AB}) \tag{8}$$

where we have introduce the unit matrix $\underline{\underline{\mathbf{1}}}$ and the square matrix $\underline{\underline{\mathbf{N}}}(\mathbf{n}_{AB})$. This square matrix, used in Eq. (8) and defined in Eq. (7), collects vector components (n_x, n_y, n_z) of $\mathbf{n}_{AB}$

$$\underline{\underline{\mathbf{N}}}(\mathbf{n}_{AB}) = \begin{pmatrix} 0 & -n_z & n_y \\ n_z & 0 & -n_x \\ -n_y & n_x & 0 \end{pmatrix} \tag{9}$$

From the Eqs. (3) and (8), it is possible to rewrite Eq. (5), in a compressed form as shown in Eq. (10) using the unit matrix $\underline{\underline{\mathbf{1}}}$ and the matrix $\underline{\underline{\mathbf{N}}}(\mathbf{n}_{AB})$

$$\underline{\mathbf{R}}_C = \underline{\mathbf{R}}_C^i + [(\cos\alpha - 1)\underline{\underline{\mathbf{1}}} + \sin\alpha\underline{\underline{\mathbf{N}}}(\mathbf{n}_{AB})]\underline{\mathbf{r}}_C^{i,AB} \tag{10}$$

On the basis of Eq. (5), the transforming $\underline{\underline{\mathbf{M}}}_{AB}(\alpha)$ matrix may be interpreted as a generator of rotation by angle α, along of the direction AB, when it is applied to $\mathbf{r}_C^i$. Its elements can be calculated using Eq. (7), from the components of the $\mathbf{n}_{AB}$ vector. The detailed expression given in Eq. (7), shows the explicit dependence of $\underline{\underline{\mathbf{M}}}_{AB}(\alpha)$ on the torsional angle α.

This concept, will be useful later in the process of dealing the matrix notation in the case of two successive rotations.

2.2. Properties of Matrix $\underline{\underline{N}}$

Given a vector $\mathbf{a} = (a_x, a_y, a_z)$, we may define the matrix $\underline{\underline{\mathbf{N}}}(\mathbf{a})$, as that matrix which contain the elements of vector $\mathbf{a}$ in the following form:

$$\underline{\underline{\mathbf{N}}}(\mathbf{a}) = \begin{pmatrix} 0 & -a_z & a_y \\ a_z & 0 & -a_x \\ -a_y & a_x & 0 \end{pmatrix} \tag{11}$$

It can be see that matrix $\underline{\underline{\mathbf{N}}}(\mathbf{a})$, defined in such a way, has the following properties:

2.2.1. Property (a)

A conventional vector addition

$$\mathbf{c} = \mathbf{a} + \mathbf{b} \tag{12a}$$

is leading to the following matrix addition:

$$\underline{\underline{\mathbf{N}}}(\mathbf{c}) = \underline{\underline{\mathbf{N}}}(\mathbf{a}) + \underline{\underline{\mathbf{N}}}(\mathbf{b}) \tag{12b}$$

The validity of this equation is shown in Eq.(12c). Note that each components of vector $\mathbf{c}$ is obtained from the addition of the corresponding components of the vectors $\mathbf{a}$ and $\mathbf{b}$:

$$\begin{pmatrix} 0 & -(a_z + b_z) & (a_y + b_y) \\ (a_z + b_z) & 0 & -(a_x + b_x) \\ -(a_y + b_y) & (a_x + b_x) & 0 \end{pmatrix} = \begin{pmatrix} 0 & -a_z & a_y \\ a_z & 0 & -a_x \\ -a_y & a_x & 0 \end{pmatrix} + \begin{pmatrix} 0 & -b_z & b_y \\ b_z & 0 & -b_x \\ -b_y & b_x & 0 \end{pmatrix} \tag{12c}$$

2.2.2. Property (b)

The product of $\underline{\underline{\mathbf{N}}}(\mathbf{a})$ matrix with a column vector $\underline{\mathbf{b}}$,

give the following results:

$$\underline{\underline{\mathbf{N}}}(\mathbf{a})\underline{\mathbf{b}} = \begin{pmatrix} 0 & -a_z & a_y \\ a_z & 0 & -a_x \\ -a_y & a_x & 0 \end{pmatrix}\begin{pmatrix} b_x \\ b_y \\ b_z \end{pmatrix} = \begin{pmatrix} a_y b_z - a_z b_y \\ a_z b_x - a_x b_z \\ a_x b_y - a_y b_x \end{pmatrix} \quad (13)$$

It should be noted, that the final column vector of Eq. (13), represents the components of the vector cross product between the vectors **a** and **b**.

It is convenient, therefore, to define

$$\mathbf{P} = \mathbf{a} \times \mathbf{b}; \qquad \underline{\mathbf{P}} = \begin{pmatrix} P_x \\ P_y \\ P_z \end{pmatrix} \quad (14)$$

where P_x, P_y and P_z has, respectively, the expressions of the elements of the last column vector at the right hand side of Eq. (13). Then, we can rewrite Eq. (13) as shown in Eq. (15)

$$\underline{\underline{\mathbf{N}}}(\mathbf{a})\underline{\mathbf{b}} = \underline{\mathbf{P}} \quad (15)$$

Substituting Eq. (7) in Eq. (5) and also applying Eq. (15), it is possible to confirm the starting Eq. (1) if we carry out the following replacements:

$$\mathbf{a} \rightarrow \mathbf{n}_{AB} \qquad \text{and} \qquad \mathbf{b} \rightarrow \mathbf{r}_C^i \quad (16)$$

2.2.3. Property (c)

Note that the application of matrix $\underline{\underline{\mathbf{N}}}(\mathbf{a})$, is meaningful if, and only if, it is applied in a column vector [see Eq. (15)].

As a consequence of the above, the product of two matrix $\underline{\underline{\mathbf{N}}}(\mathbf{a})$ and $\underline{\underline{\mathbf{N}}}(\mathbf{b})$ when applied to a $\underline{\mathbf{c}}$ vector must be executed as shown in Eq. (17)

$$\underline{\underline{\mathbf{N}}}(\mathbf{a})\underline{\underline{\mathbf{N}}}(\mathbf{b})\underline{\mathbf{c}} = \underline{\underline{\mathbf{N}}}(\mathbf{a})[\underline{\underline{\mathbf{N}}}(\mathbf{b})\underline{\mathbf{c}}] \quad (17)$$

In Eq. (17) the product $\underline{\underline{\mathbf{N}}}(\mathbf{b})\underline{\mathbf{c}} = \underline{\mathbf{P}}_1$ where $\underline{\mathbf{P}}_1$ is the column vectors which represent the cross product

$$\mathbf{P}_1 = \mathbf{b} \times \mathbf{c} \quad (18)$$

Thus, we can write the Eq. (17) as follows:

$$\underline{\underline{\mathbf{N}}}(\mathbf{a})[\underline{\underline{\mathbf{N}}}(\mathbf{b})\underline{\mathbf{c}}] = \underline{\underline{\mathbf{N}}}(\mathbf{a})\underline{\mathbf{P}}_1 \quad (19)$$

Using the property shown in Eq. (15), we can see that Eq. (19) represents the column vector of the vector cross product

$$\mathbf{P}_2 = \mathbf{a} \times \mathbf{P}_1 = \mathbf{a} \times (\mathbf{b} \times \mathbf{c}) \quad (20)$$

In contrast to Eq. (17) the matrix product $\underline{\underline{\mathbf{N}}}(\mathbf{b})[\underline{\underline{\mathbf{N}}}(\mathbf{a})\underline{\mathbf{c}}]$ represent an other vector: the cross product vector $\mathbf{b} \times (\mathbf{a} \times \mathbf{c}) = \mathbf{a} \times (\mathbf{b} \times \mathbf{c}) + \mathbf{c} \times (\mathbf{a} \times \mathbf{b})$ which is different from Eq. (18).Thus, the conclusion is that Eq. (15), representing a column vector obtained from the cross product of the three vectors involved in the order: **a**, **b** and **c**, is the correct expression. This clearly indicates the non-commutativity of the $\underline{\underline{\mathbf{N}}}$ matrices as a consequence of non- commutative rules of the cross product of three vectors. In other words; in a given order, one result is obtained while in an other order, different result is obtained. Thus

$$\mathbf{a} \times (\mathbf{b} \times \mathbf{c}) \neq \mathbf{b} \times (\mathbf{a} \times \mathbf{c})$$

hence

$$\underline{\underline{\mathbf{N}}}(\mathbf{a})[\underline{\underline{\mathbf{N}}}(\mathbf{b})\underline{\mathbf{c}}] \neq \underline{\underline{\mathbf{N}}}(\mathbf{b})[\underline{\underline{\mathbf{N}}}(\mathbf{a})\underline{\mathbf{c}}]$$

2.3. A double rotation in matrix notation

Let us consider now the case of two successive rotations. The atoms C and D rotate by α about the AB direction and atom D rotates by β about the BC direction. This situation is shown in schematic way in Fig. 2.

We define

$$\underline{\mathbf{R}}_D = \begin{pmatrix} x_D \\ y_D \\ z_D \end{pmatrix} \qquad \underline{\mathbf{R}}_D^i = \begin{pmatrix} x_D^i \\ y_D^i \\ z_D^i \end{pmatrix} \qquad \underline{\mathbf{r}}_D^{i,AB} = \begin{pmatrix} r_{Dx}^{i,AB} \\ r_{Dy}^{i,AB} \\ r_{Dz}^{i,AB} \end{pmatrix}$$

$$\underline{\mathbf{r}}_D^{BC} = \begin{pmatrix} r_{Dx}^{BC} \\ r_{Dy}^{BC} \\ r_{Dz}^{BC} \end{pmatrix} \quad (21)$$

As may be seen from Fig. 2, atom D first rotates by angle α around direction AB (with a revolution radius $\mathbf{r}_D^{AB}$ and center O_D^{AB} along this direction) and subsequently by angle β about direction BC (with a revolution radius $\mathbf{r}_D^{BC}$ and other center of rotation: O_D^{BC}).

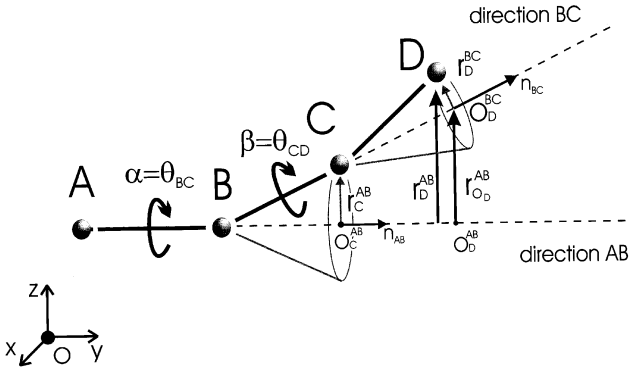

Fig. 2. Vector model for a double rotation first by α about the direction AB and subsequently by β about the direction BC. The position vectors with respect to the arbitrary origin are not shown explicitly. All symbols are defined in the text.

Also, it is interesting note that the direction BC (defined by the unit vector $\mathbf{n}_{BC} = (\mathbf{R}_C - \mathbf{R}_B)/|\mathbf{R}_C - \mathbf{R}_B|$), changes, in orientation, with the rotation of atom C with angle α. This means that $\mathbf{r}_D^{BC}$ is a vector which is related, in an explicit way, to the first torsional angle (α).

Using the concepts discussed previously for a single rotation, it is possible to write the matrix equation for the column vector position $\underline{\mathbf{R}}_D(\alpha,\beta)$ after rotation by α and β, as follows:

$$\underline{\mathbf{R}}_D(\alpha,\beta) = \underline{\mathbf{R}}_D^{i} + \underline{\underline{\mathbf{M}}}_{AB}(\alpha)\underline{\mathbf{r}}_D^{i,AB} + \underline{\underline{\mathbf{M}}}_{BC}(\alpha,\beta)\underline{\mathbf{r}}_D^{BC}(\alpha) \tag{22}$$

where we define

$$\begin{aligned}\underline{\underline{\mathbf{M}}}_{AB}(\alpha) &= (\cos\alpha - 1)\underline{\underline{\mathbf{1}}} + \underline{\underline{\mathbf{N}}}\,(\mathbf{n}_{AB})\sin\alpha \\ \underline{\underline{\mathbf{M}}}_{BC}(\alpha,\beta) &= (\cos\beta - 1)\underline{\underline{\mathbf{1}}} + \underline{\underline{\mathbf{N}}}(\mathbf{n}_{BC})\sin\beta\end{aligned} \tag{23}$$

Note that the $\underline{\underline{\mathbf{M}}}_{BC}(\alpha,\beta)$ matrix is explicitly depending on β. However, it is related, in an implicit manner, to the torsional angle α because the $\mathbf{n}_{BC}$ direction is changing with this angle of revolution (α) and therefore their components are also changing accordingly. Note that in Eq. (22) we expressed the $\mathbf{r}_D^{BC}$ dependency on α in the same way as it has been expressed previously. If angle α is taken at a fixed value, then $\mathbf{n}_{BC}$ and $\mathbf{r}_D^{BC}(\alpha_{fixed})$ are constants for all values of angle β. In this case, $\underline{\underline{\mathbf{M}}}_{BC}(\alpha_{fixed},\beta)$ is function only of the second torsional angle and has the same meaning as that of $\underline{\underline{\mathbf{M}}}_{AB}(\alpha)$.

The expression for $\underline{\underline{\mathbf{N}}}(\mathbf{n}_{BC})$ with $\mathbf{n}_{BC}$ variable with rotation angle α, is obtained from Eq. (11) as shown in Eq. (24)

$$\underline{\underline{\mathbf{N}}}(\mathbf{n}_{BC}) = \begin{pmatrix} 0 & -n_{BCz}(\alpha) & n_{BCy}(\alpha) \\ n_{BCz}(\alpha) & 0 & -n_{BCx}(\alpha) \\ -n_{BCy}(\alpha) & n_{BCx}(\alpha) & 0 \end{pmatrix} \tag{24}$$

where we express each component of $\mathbf{n}_{BC}$ as function of rotational angle α.

From the definition of $\mathbf{n}_{BC}$, it is possible to find the dependence on α

$$\mathbf{n}_{BC} = (\mathbf{R}_C - \mathbf{R}_B)/|\mathbf{R}_C - \mathbf{R}_B| = (\mathbf{R}_C - \mathbf{R}_B)/L_{BC} \tag{25}$$

where $L_{BC} = |\mathbf{R}_C - \mathbf{R}_B|$ is the length of the BC bond. Eq. (25) can be written in matrix notation using Eq. (8) for the rotation of atom C. Thus

$$\begin{aligned}\underline{\mathbf{n}}_{BC}(\alpha) = \underline{\mathbf{n}}_{BC}^{i} + \{[(\cos\alpha - 1)\underline{\underline{\mathbf{1}}} \\ + \underline{\underline{\mathbf{N}}}(\mathbf{n}_{AB})\sin\alpha]/L_{BC}\}\underline{\mathbf{r}}_C^{i,AB}\end{aligned} \tag{26}$$

where $\mathbf{n}_{BC}^{i}$ is the initial unity vector which points out award from O_D^{BC} in the BC direction before atom C revolves by α. Furthermore $\mathbf{r}_C^{i,AB}$ is the initial revolution radial vector for atom C when rotated about direction AB

$$\underline{\mathbf{r}}_C^{i,AB} = \begin{pmatrix} r_{Cx}^{i,AB} \\ r_{Cy}^{i,AB} \\ r_{Cz}^{i,AB} \end{pmatrix} \tag{27}$$

Using *Property (a)* and *Property (b)*, we can

express $\underline{\underline{\mathbf{N}}}(\mathbf{n}_{BC})$ as a matrix addition

$$\underline{\underline{\mathbf{N}}}(\mathbf{n}_{BC}) = \underline{\underline{\mathbf{N}}}(\mathbf{n}^{i}_{BC}) + [(\cos\alpha - 1)/L_{BC}]\underline{\underline{\mathbf{N}}}(\mathbf{r}^{i,AB}_{C}) + [(\sin\alpha)/L_{BC}]\underline{\underline{\mathbf{N}}}(\mathbf{P}^{i,AB}_{C}) \quad (28)$$

Eq. (28) shows an explicit dependence of matrix $\underline{\underline{\mathbf{N}}}(\mathbf{n}_{BC})$ on the first torsional angle (α). Each $\underline{\underline{\mathbf{N}}}$ matrix has the features shown in Eq. (11) and for the last term, the following equivalence must be noted

$$\mathbf{P}^{i,AB}_{C} = \mathbf{n}_{AB} \times \mathbf{r}^{i,AB}_{C} \quad (29)$$

Eq. (28) indicates that the respective matrix elements of $\underline{\underline{\mathbf{N}}}$ ($\mathbf{n}^{i}_{BC}$), $\underline{\underline{\mathbf{N}}}(\mathbf{r}^{i,AB}_{C})$ and $\underline{\underline{\mathbf{N}}}(\mathbf{P}^{i,AB}_{C})$ can be calculated from the initial position of atom C. The relationship with the torsional angle α on matrix $\underline{\underline{\mathbf{N}}}(\mathbf{n}_{BC})$, is determined by two trigonometric factors $(\cos\alpha - 1)$ and $\sin\alpha$.

Substituting Eq. (28) in Eq. (23), it is possible to obtain a more developed expression of Eq. (22)

$$\underline{\mathbf{R}}_{D}(\alpha,\beta) = \underline{\mathbf{R}}^{i}_{D} + [(\cos\alpha - 1)\underline{\underline{\mathbf{1}}} + \underline{\underline{\mathbf{N}}}(\mathbf{n}_{AB})\sin\alpha]\underline{\mathbf{r}}^{i,AB}_{D} + \{(\cos\beta - 1)\underline{\underline{\mathbf{1}}} + \sin\beta[\underline{\underline{\mathbf{N}}}(\mathbf{n}^{i}_{BC}) + [(\cos\alpha - 1)/L_{BC}]\underline{\underline{\mathbf{N}}}(\mathrm{r}^{i,AB}_{C}) + [(\sin\alpha)/L_{BC}]\underline{\underline{\mathbf{N}}}(\mathbf{P}^{i,AB}_{C})\}\underline{\mathbf{r}}^{BC}_{D}(\alpha) \quad (30)$$

This equation might be completed using the final analytical expression of $\mathbf{r}^{BC}_{D}(\alpha)$.

Fig. 2 shows that the revolution radius $\mathbf{r}^{BC}_{D}(\alpha)$ is obtained from the following equation:

$$\mathbf{r}^{BC}_{D}(\alpha) = \mathbf{R}_{D}(\alpha) - \mathbf{R}_{O^{BC}_{D}}(\alpha) \quad (31)$$

where $\mathbf{R}_{D}(\alpha)$ is the vector position of atom D and $\mathbf{R}_{O^{BC}_{D}}(\alpha)$ is the position vector of the revolution center O^{BC}_{D} of atom D with respect to the direction BC. The relationship with α takes place because the position vector of atom D and direction BC are related to the first torsional angle (α). Thus, like direction BC is rotating, it is evident that the center O^{BC}_{D} is also rotating with revolution radius $\mathbf{r}_{O^{AB}_{D}}$.

The equations governing the trajectories of atom D and center O^{BC}_{D} with respect to α angle, are similar and we can write Eq. (31) in a matrix form as

$$\underline{\mathbf{r}}^{BC}_{D}(\alpha) = \underline{\mathbf{r}}^{i,BC}_{D} + \underline{\underline{\mathbf{M}}}_{AB}(\alpha)[\underline{\mathbf{r}}^{i,AB}_{D} - \underline{\mathbf{r}}^{i,AB}_{OD}] = \underline{\mathbf{r}}^{i,BC}_{D} + \underline{\underline{\mathbf{M}}}_{AB}(\alpha)\underline{\Delta\mathbf{r}}^{i,AB}_{D} \quad (32)$$

where we define

$$\underline{\mathbf{r}}^{i,AB}_{OD} = \begin{pmatrix} r^{i,AB}_{O^{x}_{D}} \\ r^{i,AB}_{O^{y}_{D}} \\ r^{i,AB}_{O^{z}_{D}} \end{pmatrix} \quad \text{and} \quad \underline{\Delta\mathbf{r}}^{i,AB}_{D} = \underline{\mathbf{r}}^{i,AB}_{D} - \mathbf{r}^{i,AB}_{O_{D}} \quad (33)$$

With the aim to substitute Eq. (32) in Eq. (30), as a first step we rewrite the Eq. (30) as Eq. (34)

$$\underline{\mathbf{R}}_{D}(\alpha\beta) = \underline{\mathbf{R}}^{i}_{D} + [(\cos\alpha - 1)\underline{\underline{\mathbf{1}}} + \underline{\underline{\mathbf{N}}}_{AB}(\mathbf{n}_{AB})\sin\alpha]\mathbf{r}^{i,AB}_{D} + [(\cos\beta - 1)\underline{\underline{\mathbf{1}}} + \underline{\underline{\mathbf{N}}}_{BC}(\mathbf{n}^{i}_{BC})\sin\beta]\underline{\mathbf{r}}^{BC}_{D}(\alpha) + \{[(\cos\alpha - 1)\sin\beta/L_{BC}]\underline{\underline{\mathbf{N}}}_{AB}(\mathbf{r}^{i,AB}_{C}) + [\sin\alpha\sin\beta/L_{BC}]\underline{\underline{\mathbf{N}}}_{AB}(\mathbf{P}^{i,AB}_{C})\}\underline{\mathbf{r}}^{BC}_{D}(\alpha) \quad (34)$$

Each term in square brackets, represent a square matrix. The first two, have the structure of the $\underline{\underline{\mathbf{M}}}$ matrix, defined in Eq. (6), and the last term has the structure of the matrix $\underline{\underline{\mathbf{N}}}$ given in Eq. (11) with zeros in its diagonal.

In order to compress this notation, let us to define the square matrix

$$\underline{\underline{\mathbf{T}}}_{AB}(\alpha,\beta) = [(\cos\alpha - 1)\sin\beta/L_{BC}]\underline{\underline{\mathbf{N}}}(\mathbf{r}^{i,AB}_{C}) + [\sin\alpha\sin\beta/L_{BC}]\underline{\underline{\mathbf{N}}}(\mathrm{P}^{i,AB}_{C}) \quad (35)$$

Using the above definition, Eq. (34) might be written in a more compact form

$$\underline{\mathbf{R}}_{D}(\alpha,\beta) = \underline{\mathbf{R}}^{i}_{D} + \underline{\underline{\mathbf{M}}}_{AB}(\alpha)\underline{\mathbf{r}}^{i,AB}_{D} + \underline{\underline{\mathbf{M}}}_{BC}(\beta)\underline{\mathbf{r}}^{BC}_{D}(\alpha) + \underline{\underline{\mathbf{T}}}_{AB}(\alpha,\beta)\underline{\mathbf{r}}^{BC}_{D}(\alpha) = \underline{\mathbf{R}}^{i}_{D} + \underline{\underline{\mathbf{M}}}_{AB}(\alpha)\underline{\mathbf{r}}^{i,AB}_{D} + [\underline{\underline{\mathbf{M}}}_{BC}(\beta) + \underline{\underline{\mathbf{T}}}_{AB}(\alpha,\beta)]\underline{\mathbf{r}}^{BC}_{D}(\alpha) \quad (36)$$

It may be observed from Eq. (36) that the position of atom D is obtained by rotating first by angle α along direction AB and then, from that position, via rotation of vector $\mathbf{r}^{BC}_{D}(\alpha)$ by an angle β (c.f. Eq. (22)).

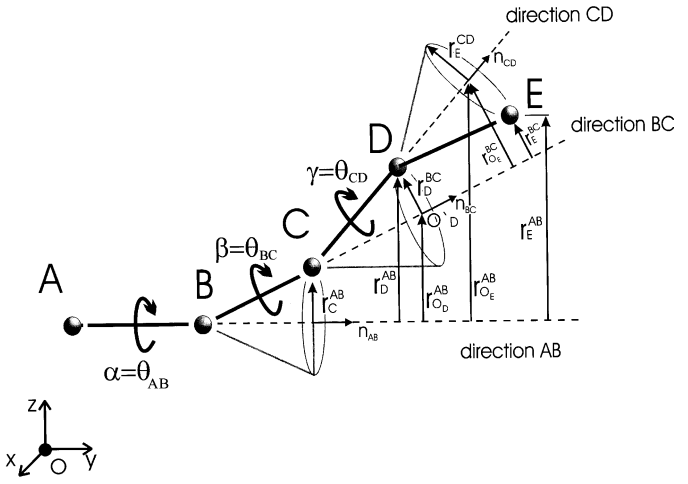

Fig. 3. Vector model for a triple rotor first by α about the direction AB, subsequently by β about the direction BC and finally by γ about the direction CD.

The term in square brackets, represent this last rotation. From Eqs. (23) and (34), we can see that $\underline{\underline{\mathbf{M}}}_{BC}(\beta)$ is the initial matrix $\underline{\underline{\mathbf{M}}}_{BC}(\alpha,\beta)$ (when $\alpha = \overline{0}^{\circ}$ and $\mathbf{n}_{BC} = \mathbf{n}^{i}_{BC}$). Thus $\underline{\underline{\mathbf{T}}}_{AB}(\alpha,\beta)$ represent the change of this matrix with the first torsional angle (α) and determine part of the total dependence of the second rotation (β) over the first rotation. The rest of the dependence, is contained in the variation of $\mathbf{r}^{BC}_{D}(\alpha)$ with the dihedral angle α. Replacing in Eq. (36) $\mathbf{r}^{BC}_{D}(\alpha)$ by its expression [given in Eq. (32)], the final equation becomes Eq. (37)

$$\underline{\mathbf{R}}_{D}(\alpha,\beta) = \underline{\mathbf{R}}^{i}_{D} + \underline{\underline{\mathbf{M}}}_{AB}(\alpha)\mathrm{r}^{i,AB}_{D} + \underline{\underline{\mathbf{M}}}_{BC}(\beta)\mathrm{r}^{i,BC}_{D} + \underline{\underline{\mathbf{T}}}_{AB}(\alpha,\beta)[\,\underline{\underline{\mathbf{M}}}_{BC}(\beta)\underline{\mathbf{r}}^{i,BC}_{D} + \underline{\underline{\mathbf{M}}}_{AB}(\alpha)\underline{\Delta\mathbf{r}}^{i,AB}_{D}] + \underline{\underline{\mathbf{M}}}_{BC}(\beta)\underline{\underline{\mathbf{M}}}_{AB}(\alpha)\underline{\Delta\mathbf{r}}^{i,AB}_{D} \quad (37)$$

In general the $\underline{\underline{\mathbf{M}}}_{PQ}(\theta)$ matrix (where θ is any dihedral angle α, β, γ, etc) applied to a initial revolution radius $\underline{\mathbf{r}}^{i}$ might be considered as those matrix generating a rotation of $\underline{\mathbf{r}}^{i}$ by θ along the direction determined by the bond PQ.

In Eq. (37) two terms (2nd and 3rd) represent rotations by angles α and β along two different directions: AB and BC, respectively like if they were completely independent to each other. The other terms (4th and 5th) are establishing the interdependence of those rotations which are modifying the BC direction and the revolution radius of the last atom along this direction. In other words: these terms determine the change of matrix $\underline{\underline{\mathbf{N}}}(\boldsymbol{n}_{BC})$, not shown explicitly in (37), and revolution radius $\mathbf{r}^{BC}_{D}$ with respect to α. It can be observed in Eq. (37) that the changes, produce vectors which are varying with both torsional angles (α and β).

Considering all the previously defined matrices, their matrix elements might be calculated from the positions of the atoms that determine the initial configuration (starting point). If we separate in each matrix, the numeric terms from the angular part, we obtain the explicit relationship with the torsional angles α and β for $\underline{\mathbf{R}}_{D}$. It is clear that the development of Eq. (37) involves matrix products. Consequently in all the cases it must be used in accordance with *Property (c)* to obtain the final result.

After dealing with rotation α and β, we can extend the development of the above equations, to the next successive torsions: γ, δ, ϵ, etc, in the case of large molecules. However, it is clear that the complexity of the mathematical expressions and their respective interpretations, will be growing as a function of the number of rotations involved. For example; in the last case we may consider to include a 5th atom, E, bonded to atom D and rotating by an angle γ along the CD direction (Fig. 3). It is possible to write to position vector $\mathbf{R}_{E}(\alpha,\beta,\gamma)$, the corresponding column

vector as follow:

$$\underline{\mathbf{R}}_{\mathrm{E}}(\alpha,\beta,\gamma) = \underline{\mathbf{R}}_{\mathrm{E}}^{\mathrm{i}} + \underline{\underline{\mathbf{M}}}_{\mathrm{AB}}(\alpha)\underline{\mathbf{r}}_{\mathrm{E}}^{\mathrm{i,AB}} + \underline{\underline{\mathbf{M}}}_{\mathrm{BC}}(\alpha,\beta)\underline{\mathbf{r}}_{\mathrm{E}}^{\mathrm{BC}}(\alpha) + \underline{\underline{\mathbf{M}}}_{\mathrm{CD}}(\alpha,\beta,\gamma)\underline{\mathbf{r}}_{\mathrm{E}}^{\mathrm{CD}}(\alpha,\beta) \quad (38)$$

where $\underline{\underline{\mathbf{M}}}_{\mathrm{CD}}(\alpha,\beta,\gamma)$ is the rotation matrix of angle γ and $\mathbf{r}_{\mathrm{E}}^{\mathrm{CD}}(\alpha,\beta)$ is the column vector which represent the radius of rotation of atom E along the direction CD. Both matrices, depend on the other angles, α and β, because these angles rotate before rotation occurs along γ. It is evident that in order to obtain a more detailed expression of Eq. (38), which express the dependence only the dihedral angles, we need to find the relationship among $\underline{\underline{\mathbf{M}}}_{\mathrm{CD}}(\alpha,\beta,\gamma)$ and $\mathbf{r}_{\mathrm{E}}^{\mathrm{CD}}(\alpha,\beta)$ with their respective torsional angles.

3. Conclusions

Probably the most interesting advantage of the equations derived, is the fact that all the numerical quantities in the matrices, can be calculated from the initial molecular configuration.

Thus, the position vectors of the atoms in the respective rotations, are analytic functions which depend only of the torsional angles. This angular dependence, allows the calculations of interatomic distances among the non-bonded atoms for arbitrary values of the dihedral angles and therefore, all the quantities which depend on them.

It should be noted that this matrix notation, would be very useful for the case of no- cyclic molecules where the dihedral angles can take a predetermined combination of values like, for example, those predicted by MCDA [4–6]. From such matrix equations one then may calculate the non-bonded interatomic distances of interest. This method should be particularly useful in studying peptide and protein folding [7] particularly in connection with predicting side chain/side chain interactions.

Acknowledgements

The research was supported by grants from the Universidad Nacional de San Luis (U.N.S.L.). Dr R. D. Enriz is a carrier researcher of Consejo Nacional de Ciencia y Tecnologia (CONICET), Republica Argentina.

References

[1] L.N. Santagata, F.D. Suvire, R.D. Enriz, L.L. Torday, I.G. Csizmadia, J. Mol. Struct. (Theochem) 465 (1999) 33–67.
[2] L.N. Santagata, F.D. Suvire, R.D. Enriz, J. Mol. Struct. (Theochem) 507 (2000) 89–95.
[3] L.N. Santagata, F.D. Suvire, R.D. Enriz, J. Mol. Struct. (Theochem) 536 (2001) 173–188.
[4] I.G. Csizmadia, General and theoretical aspects of the thiol group, The Chemistry of the Thiol Group, The Chemistry of Functional Groups, Wiley, New York, 1974 pp. 1–109.
[5] I.G. Csizmadia, Multidimensional theoretical stereochemistry and conformational potential energy surface topology, New Theoretical Concepts for Undestanding Organic Reactions, Reidel, Dordrecht, The Netherlands, 1989 pp. 1–31.
[6] J.G. Angyan, R. Daudel, A. Kucssman, I.G. Csizmadia, Chem. Phys. Lett. 136 (1987) 1.
[7] G.A. Chasse, A.M. Rodriguez, M.L. Mak, E. Derety, A. Perczel, C.P. Sosa, R.D. Enriz, I.G. Csizmadia, J. Mol. Struct. (Theochem) 537 (2001) 319–361.