

DESCRIPTION OF THE CONFORMATIONS OF COMPLEX MOLECULES BY MEANS OF DUAL QUATERNIONS

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This paper discusses a mathematical model for the geometric description of the conformations of molecules in terms of internal rotation angles, valence angles, and bond lengths by means of elementary quaternion algebra and screw calculus.

The need for a mathematical model to describe the conformation of molecules in terms of valence angles, bond lengths, and internal rotation angles arises in connection with investigations of many complex molecules, particularly biopolymers [1-6]. Eyring's matrix model [7] is usually used for this purpose. It has advantage of relative simplicity, but the description of conformations with its aid complicates the mechanical interpretation of many problems, particularly the assignment of interaction between individual atoms and the functional groups of the molecule.

The model discussed below has certain advantages, particularly in the last sense, over Eyring's model. The "kinematic visualization" of the description of molecular conformations with the aid of the new model is also an important feature.

The model to which we refer is designed for certain kinematics problems and uses the elements of screw calculus [8] and quaternion algebra [9]. We recall that a quaternion of the form

$$Q = \cos \varphi + \bar{a} \sin \varphi \tag{1}$$

is the operator of rotation around the vector \bar{a} . If instead of the real angle φ we introduce the dual angle $\Phi = \varphi + \omega \varphi^0$ (here ω is the "Clifford symbol"; $\omega^2 = 0$), the quaternion (1) will be the operator of screw transfer with axis \bar{a} and parameter φ^0/φ . We will call such a quaternion a dual quaternion and denote it by a tilde.

Let a system of rectangular coordinates be associated with the atom X_l of some molecule in such a way that its origin coincides with the center of this atom and the unit vectors \bar{j} and \bar{k} are directed respectively along the bond $X_l - X_{l+1}$ and perpendicular to the bonds $X_l - X_{l+1}$ and $X_l - X_{l-1}$, as shown in the figure. We denote the valence angles at X_l by φ_l , the angles of internal rotation around the bonds $X_l - X_{l+1}$ by ψ_l , and the lengths of these bonds by ψ_l^0 . The unit vectors directed along these bonds we denote by \bar{s}_l , while \bar{r}_l denotes the unit vectors passing through the center of X_l in the direction $\bar{s}_{l-1} \times \bar{s}_l$. Obviously, $\bar{j} = \bar{s}_l$ and $\bar{k} = \bar{r}_l$. Then,

$$\begin{aligned} \bar{r}_{l+1} &= (\cos \Psi_l + \bar{s}_l \sin \Psi_l) \bar{r}_l = \\ &= \bar{k} \cos \Psi_l + \bar{i} \sin \Psi_l = \bar{Q}_l \bar{r}_l. \end{aligned}$$

Here, $\Psi_l = \psi_l + \omega \psi_l^0$.

In its turn

$$\begin{aligned} \bar{s}_{l+1} &= (\cos \varphi_{l+1} + \bar{r}_{l+1} \sin \varphi_{l+1}) \bar{s}_l = \\ &= \bar{j} \cos \varphi_{l+1} - \bar{i} \cos \Psi_l \sin \varphi_{l+1} + \\ &+ \bar{k} \sin \Psi_l \sin \varphi_{l+1} = Q_l \bar{s}_l, \end{aligned}$$

whence,

$$\begin{aligned} \bar{r}_{l+2} &= (\cos \Psi_{l+1} + \bar{s}_{l+1} \sin \Psi_{l+1}) \bar{r}_{l+1} = \\ &= \bar{i} (\sin \Psi_l \cos \Psi_{l+1} - \cos \Psi_l \sin \Psi_{l+1} \cos \varphi_{l+1}) + \\ &+ \bar{j} \sin \Psi_{l+1} \sin \varphi_{l+1} + \bar{k} (\cos \Psi_l \cos \Psi_{l+1} - \\ &- \sin \Psi_l \sin \Psi_{l+1} \cos \varphi_{l+1}) = \bar{Q}_{l+1} \bar{Q}_l \bar{r}_l, \end{aligned}$$

and so on.

If the chain is closed we have the relationships

$$\prod_{i=1}^n \bar{Q}_i = 1; \quad \prod_{i=1}^n Q_i = 1,$$

called the closure equations [10]. They can obviously also be put in the form

$$\prod_{j=1}^k \bar{Q}_j^* = \prod_{i=k+1}^n \bar{Q}_i; \quad \prod_{j=1}^k Q_j^* = \prod_{i=k+1}^n Q_i. \tag{2}$$

Here Q^* is the quaternion conjugate to Q : $Q^* = \cos \varphi - \bar{a} \sin \varphi$. The closure equation in such form can be used to determine some of the unknown parameters (the internal rotation angles, for instance) if the rest are assigned in such a way that the total number of degrees of freedom does not exceed 6 (the so-called Grobler criterion). For this we have to obtain expressions for all \bar{s}_i , for instance, and substitute them in (2). Then, equating the scalar parts and the coefficients of \bar{j} , \bar{i} , \bar{k} on the left and right, we obtain four dual equations, which break up into eight real ones. Their solution, however, usually presents great difficulties and, hence, in the case of such problems it is better to resort to approximate methods.

If approximate values of Ψ_i and φ_i are substituted in (2), the equality is destroyed, and the discrepancy

$$\prod_{j=1}^k \bar{Q}_j^* - \prod_{i=k+1}^n \bar{Q}_i = \Xi_k$$

will also be a dual quaternion.

The expression

$$\Theta_k = 1 + \Xi_k \left[\prod_{i=j+1}^n \bar{Q}_i \right]^*$$

is a quaternion combining the vectors \bar{s}_k^j and \bar{s}_k^i , obtained by the action of the right and left parts of (2), respectively, on \bar{s}_1 .

If the scalar part of Θ_k is equal to unity there is no discrepancy. Hence, by minimizing, for instance, the function

$$P_k = (1 - \theta)^2 + (\theta^0)^2, \quad (3)$$

we can obtain values of the parameters which interest us.

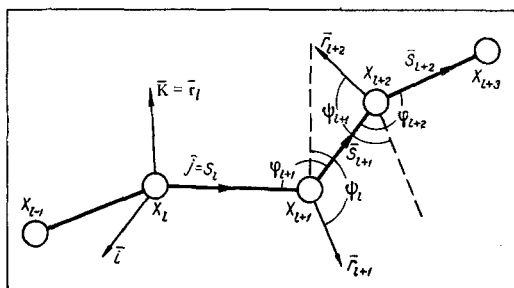


Fig. 1. Schematic description of conformation of molecule in terms of valence angles, bond lengths, and internal rotation angles.

It is important to note here that the extreme function need not necessarily have the form (3); in particular, it may be the strain energy of some element (or elements) of the chain, expressed in terms of known potentials written in dual coordinates.

To minimize P_k we can use, for instance, the method of fastest descent: by successively altering the variables by small amounts $\Delta\psi_i$ we obtain increments ΔP_k and from them, approximate values of the partial derivatives: $\frac{\partial P_k}{\partial \psi_i} \approx \frac{\Delta P_k}{\Delta \psi_i}$. Corrections for each ψ_i are found from the formula

$$u_i = \frac{-P_k \left(\frac{\partial P_k}{\partial \psi_i} \right)}{\sqrt{\sum_i \left(\frac{\partial P_k}{\partial \psi_i} \right)^2}}.$$

Function P_k , generally speaking, can have several minima and, hence, success largely depends on the choice of the initial values of ψ_i . In many cases of interest, however, the choice of approximate values can be made with sufficient accuracy.

Many complex structures, particularly the secondary and tertiary structure of proteins, can be regarded as a combination of articulated spatial chains of the described type. The conditions for their closure are formulated in a similar way, and if P_k is additive, ΣP_k is minimized. Calculation of the derivatives in this case is only slightly complicated, since each ψ_i is contained in two, rarely more, chains.

In conclusion we must mention the possibility of stress analysis in complex structures in terms of screw calculus. Each bond (or other rigid element which can be regarded as a link) is acted on by 2-4 screw forces. The sum of these screw forces together with the sum of the moments of their main parts relative to any point of application of a must be zero:

$$\sum_i \bar{F}_i + \sum_j \mu_a (\bar{f}_j) = 0.$$

If we can obtain expressions for the screw forces which produce a certain deformation we can, knowing the spatial structure of the molecule, obtain an idea of the stresses on its individual bonds. Estimates of this kind may be of interest, if not from the computational aspect, then at least as a method of demonstrating the "statics" of the molecule.

It is from the viewpoint of various static models that the above-described model is of greatest interest; in particular, we can expect that models of such kind may be useful in connection with the examination of the properties of some polymers. It is known, for instance, that the melting point, elasticity, solubility, and other properties of polyamides are determined by the mutual arrangement and orientation of the interacting functional groups [11]. A significant factor in this case is not only the degree of saturation of the hydrogen bonds, but the fact that in several cases, owing to the unfavorable spatial disposition of the amide groups, some of the hydrogen bonds formed by them are deformed. This deformation can be evaluated by comparing the molecular and crystallographic parameters by means of the described model.

Of course, the results obtained with this model, like the results obtained by means of Eyring's model [1-6], can be regarded only as exploratory. Since information of such kind is unattainable, or almost unattainable by experiment, theoretical methods like the one described are now being adopted.

REFERENCES

1. M. O. Dayhoff, J. Am. Chem. Soc., **86**, 2295, 1964.
2. C. Ramakrishnan, Proc. Ind. Ac. Sci., **A59**, 327, 1964.
3. G. Nemethy and H. A. Scheraga, Biopolymers, **3**, 155, 1965.
4. G. N. Ramachandran, Abstr. 10-th ann. Meet. Bioph. Soc., 1966.
5. S. I. Leach, G. Nemethy, and H. A. Scheraga, Biopolymers, **4**, 369, 1966.
6. H. A. Scheraga, S. I. Leach, R. A. Scott, and G. Nemethy, Disc. Far. Soc., no. 40, 268, 1965.
7. H. Eyring, Phys. Rev., **39**, 746, 1932.
8. F. M. Dimentberg, Screw Calculus [in Russian], Nauka, Moscow, 1965.
9. W. Blaschke, Ann. Acad. Sci. Fen., AI, 250/3, 1958.
10. A. T. Yang and F. Freidenshtein, Prikl. mekh., **31**, no. 2, 1964.
11. V. V. Korshak and T. M. Frunze, Synthetic Heterochain Polyamides [in Russian], GKhI, Moscow, 1962.