AUTOMATIC OPTIMIZATION OF THE SPACE ARRANGEMENT OF TWO MOLECULES CONTROLLED BY THE BUCKINGHAM POTENTIAL

Z. SLANINA

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 121 38 Prague 2

Received April 30th, 1974

A method is presented, which permits automatic optimization of the space arrangement of two interacting molecules. The Buckingham potential is assumed and the optimization is performed by minimization of the interaction energy by the variable metric method making use of explicit formulas for the first derivatives of energy. A coordinate system used permits a straightforward generalization to clusters of any number of interacting molecules.

Empirical interaction potentials are widely used for estimations of intra- and intermolecular interaction energies, in particular in searching for the optimal conformation of a molecular skeleton[1] or in studies of clusters containing two or more molecules[2]. Among the many successful conformational studies let us recall the estimation of the torsion angle in biphenyl[3], racemization of *ortho*-substituted biphenyls[4], and the studies of alicyclic compounds by Hendrickson[5,6]. These results suggested to us that it might be reasonable to apply the empirical potentials to studies of molecular complexes, particularly in the gas phase.

All applications of empirical potentials mentioned above involve a common initial step, *viz.* the search for a configuration of atoms in a molecule or molecules in a cluster in which the energy is at minimum with respect to all coordinates of the system. The most widely used way of energy minimization is based on the tabulation of the energy function for discrete values of coordinates. This procedure cannot be considered entirely satisfactory because of both the extent of necessary calculations and the accuracy achieved. A more elegant approach to the minimization problem was reported by Wiberg[7], who constructed the first derivatives of energy from equidistant shifts of all atomic coordinates; a subsequent approach to the optimum was generated by the steepest descent method.

This paper presents a method permitting optimization of the space arrangement of two molecules for the Buckingham-type interaction potential[1] on the basis of accurate first derivatives of energy. The procedure makes use of the iterative variable metric method, which was introduced into the theoretical chemistry by McIver and Komornicki[8] for purposes of automatic geometry optimization by semiempirical quantum chemical methods.

POTENTIAL USED

For the case of two interacting molecules of N_1 and N_2 atoms the Buckingham potential possesses the following form[1]:

$$V = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} - C_{ij}^{(1)}(R_i^0 + R_j^0)^6/R_{ij}^6 + C_{ij}^{(2)} \exp\left(-C^{(3)}R_{ij}/(R_i^0 + R_j^0)\right). \qquad (1)$$

Here $C_{ij}^{(1)}$, $C_{ij}^{(2)}$, and $C^{(3)}$ are empirical constants, R_i^0, R_j^0 atomic van der Waals radii, R_{ij} the distance between the i th atom of the one molecule and the j th atom of the other. Hence, potential (*1*) is a function of $N_1 \,.\, N_2$ variables R_{ij}.

COORDINATE SYSTEM

It is convenient to use as small a coordinate basis set as possible, *i.e.* to limit oneself to a set of independent coordinates. Let us assume that the geometry of any of interacting molecules is identical with that of the isolated molecule. Provided the two rigid molecules are nonlinear, their mutual orientation can unambigously be determined by means of mere six independent parameters, in contrast to $N_1 \,.\, N_2$ variables appearing in Eq. (*1*). In order to have a facile insight into the course of the interaction, it is desirable that the six parameters be so chosen as to have a simple geometrical meaning.

Let the molecule 1 be fixed in the coordinate system $x^{(1)}y^{(1)}z^{(1)}$, the molecule 2 in the system $x^{(2)}y^{(2)}z^{(2)}$. The atomic coordinates in the respective fixed coordinate systems remain unchanged in the course of optimization. The arrangement of the two systems relative to each other varies, of course, and can be described by means of the following terms:

I. x_0, y_0, z_0 denoting the origin of the $x^{(2)}y^{(2)}z^{(2)}$ system in the $x^{(1)}y^{(1)}z^{(1)}$ system.
II. Euler angles ϑ, φ, χ, being determined by the $x^{(1)}y^{(1)}z^{(1)}$ and $x^{(2)}y^{(2)}z^{(2)}$ axes and defined as in ref.[9].

The coordinates of any atom of the molecule 2 in the $x^{(1)}y^{(1)}z^{(1)}$ system can be expressed by means of its known coordinates in the $x^{(2)}y^{(2)}z^{(2)}$ system and variables x_0, y_0, z_0, ϑ, φ, and χ; the formulas are listed in Appendix.

GRADIENT OF THE INTERACTION ENERGY AND THE ITERATIVE PROCEDURE

Derivatives of potential (*1*) with respect to variables x_0, y_0, z_0, ϑ, φ, and χ are components of the gradient of interaction energy

$$\mathbf{g} \equiv [\partial V/\partial x_0, \partial V/\partial y_0, \partial V/\partial z_0, \partial V/\partial \vartheta, \partial V/\partial \varphi, \partial V/\partial \chi] \qquad (2)$$

and are given by the expression such as

$$\partial V/\partial x_0 = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} (\partial V/\partial R_{ij})(\partial R_{ij}/\partial x_0)\,. \tag{3}$$

Their explicit formulas (see Appendix) in conjugation with a suitable iteration technique permit an effective search for points on hypersurface (*1*) with zero first derivatives.

Let $\boldsymbol{q}_i$ denote a vector of x_0, y_0, z_0, ϑ, φ, and χ parameters given in the i th iteration and $\boldsymbol{g}_i$ the respective gradient (*2*). Then the $(i + 1)$th approach to the optimal six parameters is given by the recursion formula[8,10]

$$\boldsymbol{q}_{i+1} = \boldsymbol{q}_i - \alpha_i \boldsymbol{A}_i \boldsymbol{g}_i\,. \tag{4}$$

$\boldsymbol{A}_i$ is a square matrix constructed according to recursion formulas given in ref.[10] and which converges to the inverse matrix of second derivatives, α_i is a damping factor so chosen as to ensure positive-definiteness of the matrix of second derivatives[10]. From $\boldsymbol{q}_{i+1}$ given by Eq. (*4*) $\boldsymbol{g}_{i+1}$ is constructed and relationship (*4*) is applied in a next step unless a required convergency criterion has already been satisfied.

APPLICATIONS AND CONCLUSIONS

A computer program was written for the relationships derived and used for a study of a series of selected systems. The parameter sets adopted for potential (*1*) were those of Eliel and collaborators[1] and Kitaygorodsky[11].

In agreement with what was claimed[8] the variable metric method was found highly effective. Since the variable metric method leads to the nearest minimum and preserves the symmetry of the starting geometry, determination of all minima on the energy hypersurface (*1*) requires the systematic variation of the starting geometry. Even with relatively simple systems, the hypersurface (*1*) may possess a series of energy minima. Treatment of the interaction of F_2 and C_2H_4, in which the parameter set of ref.[1] was used, gave 10 stationary points with very close values of interaction energy. In the case with the system of I_2 and C_6H_6, both parametrizations yielded 9 stationary points in close correspondence.

The formalism employed permits a straightforward generalization of the automatic optimization to systems containing N interacting molecules; in this case $6(N\text{-}1)$ coordinates are to be optimized.

APPENDIX

First Derivatives of the Buckingham Potential with Respect to Variables x_0, y_0, z_0, ϑ, φ, χ

Let us introduce the following notation:

$x_i^{(1)}$, $y_i^{(1)}$, $z_i^{(1)}$ denote the Cartesian coordinates of the ith atom of the first molecule in the $x^{(1)}\,y^{(1)}\,z^{(1)}$ system fixed with the first molecule

$x_j^{(2)}, y_j^{(2)}, z_j^{(2)}$ denote the Cartesian coordinates of the jth atom of the second molecule in the $x^{(2)}\ y^{(2)}\ z^{(2)}$ system fixed with the second molecule

$x_j^{(1)}, y_j^{(1)}, z_j^{(1)}$ denote the Cartesian coordinates of the jth atom of the second molecule in the $x^{(1)}\ y^{(1)}\ z^{(1)}$ system.

It holds[9]

$$x_j^{(1)} = x_0 + x_j^{(2)} (\cos\vartheta \cos\varphi \cos\chi - \sin\varphi \sin\chi) - y_j^{(2)} (\cos\vartheta \cos\varphi \sin\chi + \sin\varphi \cos\chi) + \\ + z_j^{(2)} \sin\vartheta \cos\varphi \tag{5}$$

$$y_j^{(1)} = y_0 + x_j^{(2)} (\cos\vartheta \sin\varphi \cos\chi + \cos\varphi \sin\chi) + y_j^{(2)} (-\cos\vartheta \sin\varphi \sin\chi + \cos\varphi \cos\chi) + \\ + z_j^{(2)} \sin\vartheta \sin\varphi \tag{6}$$

$$z_j^{(1)} = z_0 - x_j^{(2)} \sin\vartheta \cos\chi + y_j^{(2)} \sin\vartheta \sin\chi + z_j^{(2)} \cos\vartheta\,. \tag{7}$$

In terms $x_j^{(1)}, y_j^{(1)}, z_j^{(1)}$ given by (5), (6), (7), the first derivatives of the Buckingham potential (1) can be expressed by the following concise formulas:

$$\partial V/\partial x_0 = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} V'_{ij}(x_j^{(1)} - x_i^{(1)}) \tag{8}$$

$$\partial V/\partial y_0 = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} V'_{ij}(y_j^{(1)} - y_i^{(1)}) \tag{9}$$

$$\partial V/\partial z_0 = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} V'_{ij}(z_j^{(1)} - z_i^{(1)}) \tag{10}$$

$$\partial V/\partial \vartheta = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} V'_{ij}((x_j^{(1)} - x_i^{(1)}) (-x_j^{(2)} \sin\vartheta \cos\varphi \cos\chi + y_j^{(2)} \sin\vartheta \cos\varphi \sin\chi + \\ + z_j^{(2)} \cos\vartheta \cos\varphi) + (y_j^{(1)} - y_i^{(1)}) (-x_j^{(2)} \sin\vartheta \sin\varphi \cos\chi + y_j^{(2)} \sin\vartheta \sin\varphi \sin\chi + \\ + z_j^{(2)} \cos\vartheta \sin\varphi) + (z_j^{(1)} - z_i^{(1)}) (-x_j^{(2)} \cos\vartheta \cos\chi + y_j^{(2)} \cos\vartheta \sin\chi - z_j^{(2)} \sin\vartheta)) \tag{11}$$

$$\partial V/\partial \varphi = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} V'_{ij}((x_j^{(1)} - x_i^{(1)}) (-x_j^{(2)} (\cos\vartheta \sin\varphi \cos\chi + \cos\varphi \sin\chi) + \\ + y_j^{(2)}(\cos\vartheta \sin\varphi \sin\chi - \cos\varphi \cos\chi) - z_j^{(2)} \sin\vartheta \sin\varphi) + (y_j^{(1)} - y_i^{(1)})\,. \\ .\,(x_j^{(2)}(\cos\vartheta \cos\varphi \cos\chi - \sin\varphi \sin\chi) - \\ - y_j^{(2)} (\cos\vartheta \cos\varphi \sin\chi + \sin\varphi \cos\chi) + z_j^{(2)} \sin\vartheta \cos\varphi)) \tag{12}$$

$$\partial V/\partial \chi = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} V'_{ij}((x_j^{(1)} - x_i^{(1)}) (-x_j^{(2)}(\cos\vartheta \cos\varphi \sin\chi + \sin\varphi \cos\chi) + \\ + y_j^{(2)}(-\cos\vartheta \cos\varphi \cos\chi + \sin\varphi \sin\chi)) + \\ + (y_j^{(1)} - y_i^{(1)}) (x_j^{(2)}(-\cos\vartheta \sin\varphi \sin\chi + \cos\varphi \cos\chi) - y_j^{(2)}(\cos\vartheta \sin\varphi \cos\chi + \\ + \cos\varphi \sin\chi)) + (z_j^{(1)} - z^{(1)}_i) (x_j^{(2)} \sin\vartheta \sin\chi + y_j^{(2)} \sin\vartheta \cos\chi))\,. \tag{13}$$

V'_{ij} appearing in (8)—(13) has the following meaning

$$V'_{ij} = 6\, C_{ij}^{(1)}(R_i^0 + R_j^0)^6/R_{ij}^8 - C_{ij}^{(2)} C^{(3)}/(R_{ij}(R_i^0 + R_j^0)) \exp(-C^{(3)} R_{ij}/(R_i^0 + R_j^0))\,. \tag{14}$$

Distance between the ith and jth atoms is

$$R_{ij} = ((x_i^{(1)} - x_j^{(1)})^2 + (y_i^{(1)} - y_j^{(1)})^2 + (z_i^{(1)} - z_j^{(1)})^2)^{1/2} . \quad (15)$$

REFERENCES

1. Eliel E. L., Allinger N. L., Angyal S. J., Morrison G. A.: *Conformational Analysis*. Interscience, New York 1965.
2. Hirschfelder J. O., Curtiss C. F., Bird R. B.: *Molecular Theory of Gases and Liquids*. Wiley, New York 1954.
3. Gołebiewski A., Parczewski A.: Acta Phys. Polon. *A37*, 879 (1970).
4. Westheimer F. H., Mayer J. E.: J. Chem. Phys. *14*, 733 (1946).
5. Hendrickson J. B.: J. Am. Chem. Soc. *83*, 4537 (1961).
6. Hendrickson J. B.: J. Am. Chem. Soc. *84*, 3355 (1962).
7. Wiberg K. B.: J. Am. Chem. Soc. *87*, 1070 (1965).
8. McIver J. W., Komornicki A.: Chem. Phys. Lett. *10*, 303 (1971).
9. Wilson E. B., Decuis J. C., Cross P. C.: *Molecular Vibrations*. McGraw-Hill, New York 1955.
10. Murtagh B. A., Sargent R. W. H.: Computer J. *13*, 185 (1970).
11. Kitaygorodsky A. I.: Tetrahedron *14*, 230 (1961).

Translated by P. Čársky.