

Note

An Improved Algorithm for Molecular Dynamics Simulation of Rigid Molecules

1. INTRODUCTION

In the past a considerable effort was devoted to obtain a well-behaved equation of motion for the rotation of rigid molecules to be used in molecular dynamics simulation [1-5]. Although the method due to Evans which is based on a quaternion parameter (QP) representation of the molecular orientation yields excellent results with small timesteps, it is impossible to reach the steplength common in constraint dynamics [6]. The obstacle which one encounters is a blow-up behaviour of the quaternions square-sum and a rapid heating of the simulated liquid.

In this paper a second-order differential equation will be communicated which is explicit in the QPs and does not suffer from the instability mentioned above. After deriving the equation of motion in the next section the numerical performance of this improved algorithm will be compared with those of other methods in Section 3.

2. THE EQUATION OF MOTION FOR THE QUATERNION PARAMETERS

According to Evans the QPs are defined in terms of Goldstein's Euler angles [7]:

$$\begin{aligned}
 \chi &= \cos(\theta/2) * \cos((\Psi + \Phi)/2) \\
 \eta &= \sin(\theta/2) * \cos((\Psi - \Phi)/2) \\
 \xi &= \sin(\theta/2) * \sin((\Psi - \Phi)/2) \\
 \zeta &= \cos(\theta/2) * \sin((\Psi + \Phi)/2).
 \end{aligned}
 \tag{1}$$

They obey the constraint

$$\mathbf{q} * \mathbf{q} = 1,
 \tag{2}$$

where $\mathbf{q} := (\xi, \eta, \zeta, \chi)^T$. The matrix \mathbf{R}

$$\mathbf{R} = \begin{pmatrix}
 -\xi^2 + \eta^2 - \zeta^2 + \chi^2 & 2(\zeta\chi - \xi\eta) & 2(\eta\zeta + \xi\chi) \\
 -2(\xi\eta + \zeta\chi) & \xi^2 - \eta^2 - \zeta^2 + \chi^2 & 2(\eta\chi - \xi\zeta) \\
 2(\eta\zeta - \xi\chi) & -2(\xi\zeta + \eta\chi) & -\xi^2 - \eta^2 + \zeta^2 + \chi^2
 \end{pmatrix}
 \tag{3}$$

rotates the laboratory system into the molecular system. The time derivative $\dot{\mathbf{g}}$ is related to the angular velocity $\boldsymbol{\omega}$ in the molecular system by the orthogonal matrix \mathbf{A} :

$$\dot{\mathbf{q}} = \frac{1}{2} \mathbf{A} \begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \\ 0 \end{pmatrix}, \quad \mathbf{A} = \begin{pmatrix} -\zeta & -\chi & \eta & \xi \\ \chi & -\zeta & -\xi & \eta \\ \xi & \eta & \chi & \zeta \\ -\eta & \xi & -\zeta & \chi \end{pmatrix}. \quad (4)$$

$\dot{\boldsymbol{\omega}}$ can be obtained from the Eulerian equations [7]

$$\begin{aligned} I_{xx} \dot{\omega}_x - \omega_y \omega_z (I_{yy} - I_{zz}) &= N_x \\ I_{yy} \dot{\omega}_y - \omega_z \omega_x (I_{zz} - I_{xx}) &= N_y \\ I_{zz} \dot{\omega}_z - \omega_x \omega_y (I_{xx} - I_{yy}) &= N_z \end{aligned} \quad (5)$$

where \mathbf{N} is the torque and I_{xx} , I_{yy} , I_{zz} are the diagonal elements of the tensor of inertia. Hence it is possible to evaluate the orientational motion using Eqs. (4) and (5) simultaneously as proposed by Evans. In conjunction with the predictor-corrector scheme due to Gear [8], however, the corrector for \mathbf{q} has to be calculated from predicted values. So a differential equation which contains only the QP seemed to be promising to remove the premature instability in Evan's method. Such an equation can be derived in the following way:

From Eq. (4) the angular velocity $\boldsymbol{\omega}$ and its time derivative $\dot{\boldsymbol{\omega}}$ can be written as

$$\begin{pmatrix} \omega_x \\ \omega_y \\ \omega_z \\ 0 \end{pmatrix} = 2 * \mathbf{A}^T \dot{\mathbf{q}}, \quad (6)$$

$$\begin{pmatrix} \dot{\omega}_x \\ \dot{\omega}_y \\ \dot{\omega}_z \\ 0 \end{pmatrix} = 2 * (\mathbf{A}^T \dot{\mathbf{q}} + \mathbf{A}^T \ddot{\mathbf{q}}). \quad (7)$$

Inserting $\dot{\boldsymbol{\omega}}$ from Eq. (7) into Eq. (5) one gets after rearranging:

$$\ddot{\mathbf{q}} = \frac{1}{2} \mathbf{A} \begin{pmatrix} (N_x + \omega_y \omega_z (I_{yy} - I_{zz})) / I_{xx} \\ (N_y + \omega_z \omega_x (I_{zz} - I_{xx})) / I_{yy} \\ (N_z + \omega_x \omega_y (I_{xx} - I_{yy})) / I_{zz} \\ -2 * (\dot{\mathbf{q}})^2 \end{pmatrix}. \quad (8)$$

The components of the angular velocity ω are related to the QP via Eq. (6). Note that the second derivative of the quaternion constraint $\mathbf{q} \cdot \mathbf{q} = 1$ appears in Eq. (8) explicitly. Hence if the constraint (2) and its time derivative are fulfilled by the initial conditions to Eq. (8), it will be so for all subsequent times except for numerical imprecision. The accumulation of this kind of error can be suppressed with the rescaling procedure described by Evans.

3. COMPARISON OF THE DIFFERENT ALGORITHMS

To study the suitability of Eq. (8), it was used in a MD-simulation of 216 ST2-molecules enclosed between two smooth walls. The details of this system and its properties are given elsewhere [9]. For the integration of the equation of motion a fifth order scheme [8] was employed. It was noted, that iterating the corrector without recalculating the forces reduces $|\mathbf{q} \cdot \mathbf{q} - 1|$ considerably while it has no effect on the energy conservation. Parallel runs with the constraint algorithm and the original QP version were conducted for comparison. Different steplengths were employed and the simulations extended over 1.2 ps. The results are given in Table I which contains the rms deviations of the total energy and its trend if it could be verified unambiguously.

The new method is being applied successfully to simulations of aqueous electrolytes [10] and liquid chloroform [11] in this laboratory. In the case of chloroform, however, it was not feasible to increase the time step beyond three times the original length. It seems that the improvement introduced by Eq. (8) is less dramatic with molecules whose tensor of inertia is more isotropic.

TABLE I
Comparison of the Different Methods

Method	Time step (ps)	rms deviation of total energy (kT)	Trend in total energy (kT/ps)
Ryckaert <i>et al.</i> [6]	$1.09 \cdot 10^{-3}$	$2.31 \cdot 10^{-2}$	$8.1 \cdot 10^{-3}$
	$2.18 \cdot 10^{-4}$	$5.6 \cdot 10^{-4}$	None
Evans [5]	$2.18 \cdot 10^{-4}$	$1.3 \cdot 10^{-4}$	None
	$> 4.00 \cdot 10^{-4}$	Not stable	
This paper	$1.64 \cdot 10^{-3}$	$2.7 \cdot 10^{-3}$	$1.1 \cdot 10^{-3}$
	$1.09 \cdot 10^{-3}$	$2.6 \cdot 10^{-4}$	None

4. CONCLUSIONS

It can be seen from Table I that the method proposed in this paper is more stable than the original QP algorithm or the constraint method, which is the one most frequently used on aqueous systems. The stability of this improved algorithm even at large steplength allows a faster MD-simulation, so whenever the extra computer memory necessary to accommodate the higher derivatives of the QP is not a problem, it is to be preferred.

Copies of the predictor and corrector subroutines written in Cray-FORTRAN may be obtained from the author on request.

REFERENCES

1. J. BAROJAS, D. LEVESQUE, AND B. QUENTREC, *Phys. Rev. A* **7** (1973), 1092.
2. P. S. Y. CHEUNG, *Chem. Phys. Lett.* **40** (1976), 19.
3. F. H. STILLINGER AND A. RAHMAN, *J. Chem. Phys.* **60** (1974), 1545.
4. D. J. EVANS, *Mol. Phys.* **34** (1977), 317.
5. D. J. EVANS AND S. MURAD, *Mol. Phys.* **34** (1977), 327.
6. J. P. RYCKAERT, G. CICCOTTI, AND H. J. C. BERENDSEN, *J. Comput. Phys.* **23** (1977), 327.
7. H. GOLDSTEIN, "Classical Mechanics," 2nd ed., Addison-Wesley, Reading, Mass., 1980.
8. C. W. GEAR, AEC Research and Development Rep. No. ANL-7126, 1966.
9. R. SONNENSCHNEIN AND K. HEINZINGER, *Chem. Phys. Lett.* **102** (1983), 550.
10. E. SPOHR, private communication.
11. W. DIETZ, private communication.

RECEIVED: March 8, 1984; REVISION: August 17, 1984.

ROLAND SONNENSCHNEIN*
Max-Planck-Institut für Chemie
(Otto-Hahn-Institut)
D-6500 Mainz, Federal Republic of Germany

* Present address: IBM Corporation, Department 48B/Bldg. 963, MS 428, P. O. Box 100, Kingston, New York 12401.