

AN ALGORITHM FOR ROTATIONAL MOTION OF RIGID MOLECULES

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Dynamic simulations of rigid polyatomic molecules often use a quaternion method[1] to integrate the rotational motion. The quaternions provide a representation of the orientation of the molecule in which the equations of motion are free of singularities. These equations have usually been integrated using a fourth-order predictor-corrector method[2]. The purpose of this article is to suggest the use of a new and simpler algorithm to integrate these equations which gives better results than the usual algorithm and is also superior to the alternative constraint method[3].

To explain our motivation we first consider the case of centre-of-mass motion. If we write the equation of motion of the COM as two first-order equations, using an obvious notation

$$\underline{\dot{V}} = \underline{F}/m \quad (1a)$$

$$\underline{\dot{R}} = \underline{V} \quad (1b)$$

and use Taylor series expansion it is easy to derive the leapfrog algorithm

$$\underline{v}^{n+1/2} = \underline{v}^{n-1/2} + \Delta t \underline{F}^n/m \quad (2a)$$

$$\underline{R}^{n+1} = \underline{R}^n + \Delta t \underline{v}^{n+1/2} \quad (2b)$$

(This algorithm is algebraically equivalent to the Verlet algorithm but computationally superior). In the following table we compare the energy conservation of the leapfrog with a high-order predictor-corrector algorithm, the Gear 4-level formula[4]. The table shows the RMS fluctuation in total energy (arbitrary units) for an argon simulation.

<u>Δt(fs)</u>	<u>10</u>	<u>20</u>	<u>30</u>
Leapfrog	12	19	27
Gear 4-level.	11	14	123

The high order algorithm performs slightly better at smaller time-

steps, but its errors increase vary rapidly at large time-steps, whereas the errors in the leapfrog increase only steadily with increasing Δt . On theoretical grounds the Gear formulae are expected to be very accurate and stable, but the theoretical analysis applies strictly only to the case of a particle moving in a fixed force field. This is not the case in a dynamic simulation where each particle moves in the fluctuating force field produced by its neighbours. The high-order algorithms predict the time derivatives of the force from its value at previous time-steps, but it would appear that this prediction is invalidated by the fluctuations in the force field in the liquid at larger time-steps, and indeed has a destabilising effect on the algorithm. This is important because we want to use as large a time-step as possible in order to sample phase space most efficiently, and the leapfrog is therefore the most suitable algorithm.

The evidence[5] indicates that in a molecular liquid the fluctuations in torque act on a very similar time-scale to the force fluctuations, suggesting that a simple low-order algorithm might also be suitable for rotational motion. The basic equations governing rotational motion are the following

$$\underline{\dot{J}} = \underline{T} \tag{3a}$$

$$\underline{\dot{J}}_p = \underline{A} \underline{J} \tag{3b}$$

$$\omega_{pi} = J_{pi} / \underline{T}_i \tag{3c}$$

$$\begin{bmatrix} \xi \\ \eta \\ \zeta \\ \dot{\chi} \end{bmatrix} = 1/2 \begin{bmatrix} -\zeta & -\chi & \eta & \xi \\ \chi & -\zeta & -\xi & \eta \\ \xi & \eta & \chi & \zeta \\ -\eta & \xi & -\zeta & \chi \end{bmatrix} \begin{bmatrix} \omega_{p1} \\ \omega_{p2} \\ \omega_{p3} \\ 0 \end{bmatrix} \tag{3d}$$

Here \underline{T} is the torque and \underline{J} the angular momentum. We obtain the components of \underline{J} in the principal axis system by means of the rotation matrix $A[1]$.

Dividing by the principal moments of inertia I_i then gives the principal components of angular velocity, which are used to obtain the time derivatives of the quaternion parameters. We re-write this last equation symbolically as

$$\dot{\underline{q}} = \underline{Q} \underline{\omega} \underline{p} \quad (3d)$$

this being an equation in a four-dimensional space.

We see immediately that (3a) has the same form as (1a) and can be integrated by a leapfrog analogous to (2a). However, the quaternion 'velocity' depends not only on \underline{q} but also on the quaternions themselves, i.e. on the orientation, both directly in (3d) and through the rotation matrix. This is a situation where a leapfrog cannot be used. To see why consider the case of the simple first-order equation

$$\dot{x} = f(x,t)$$

A leapfrog for this equation would have the form

$$x^{n+1/2} = x^{n-1/2} + \Delta t f(x^n, t^n)$$

$$x^{n+1} = x^n + \Delta t f(x^{n+1/2}, t^{n+1/2})$$

where both the 'step' and 'mid-step' co-ordinates are required since x appears in the equation for x . The problem with this algorithm is that the step and mid-step equations are only weakly coupled through the velocity term; numerical errors cause them to decouple and we get two solutions which oscillate unstably about the correct solution. The remedy is to use the following method[6]. An auxiliary equation propagates x from n to $n+1/2$ using a first-order Taylor expansion

$$x^{n+1/2} = x^n + \frac{1}{2} \Delta t f(x^n, t^n)$$

and the main equation leapfrogs from n to $n+1$, employing $x^{n+1/2}$ in the velocity terms

$$x^{n+1} = x^n + \Delta t f(x^{n+1/2}, t^{n+1/2})$$

The first-order mid-step coordinate $x^{n+1/2}$ has an auxiliary role only and is not saved. Overall, the algorithm is second-order accurate.

We thus arrive at the following algorithm for rotational motion.

Auxiliary part

1. $\underline{J}^n = \underline{J}^{n-1/2} + \frac{1}{2} \Delta t \underline{T}^n$
2. $\underline{J}_p^n = \underline{A}^n \underline{J}^n$
3. $\omega_{pi}^n = J_{pi}^n / I_i$
4. $\underline{Q}^{n+1/2} = \underline{Q}^n + \frac{1}{2} \Delta t \underline{Q}^n \underline{\omega}_p^n$
5. Use $\underline{Q}^{n+1/2}$ to calculate $\underline{A}^{n+1/2}$ and $\underline{Q}^{n+1/2}$

Main part

6. $\underline{J}^{n+1/2} = \underline{J}^{n-1/2} + \Delta t \underline{T}^n$
7. $\underline{J}_p^{n+1/2} = \underline{A}^{n+1/2} \underline{J}^{n+1/2}$
8. $\omega_{pi}^{n+1/2} = J_{pi}^{n+1/2} / I_i$
9. $\underline{Q}^{n+1/2} = \underline{Q}^n + \Delta t \underline{Q}^{n+1/2} \underline{\omega}_p^{n+1/2}$
10. Store $\underline{J}^{n+1/2}$ and \underline{Q}^{n+1} for the next step.

The following table compares the energy conservations of this algorithm with the fourth-order predictor-corrector, and also with the constraint method. In the latter case the 'free-flight' phase uses a leapfrog, and so we might expect similar behaviour to the new algorithm. The quantity tabulated is the RMS fluctuation in total energy expressed as a percentage

of the fluctuation in potential energy, and the system is a three-centre model for cyclopropane[7].

$\Delta t(\text{fs})$	6	8	10	12
New algorithm	2.6	4.7	9.7	20
Constraints	2.8	2.8	12.4	37
4th order p.c.	4.0	4.2	23.6	85

We see as expected that although the fourth-order algorithm is accurate at small time-steps, its errors increase much more rapidly as the time-step increases than do those of the suggested new algorithm, which is also better in this respect than the constraint algorithm. Further advantages of the new algorithm are that it is simple, needs minimal storage (three components of \underline{J} and four of \underline{g}) and is self-starting.

Finally, we note that diatomics are a special case. If the constraint method is used the equation for the single constraint force is a quadratic and hence exactly soluble, whereas in the polyatomic case the equations of constraint must be linearised and iterated. On the other hand, the four quaternions with the usual single constraint over-determine the problem since there are only two degrees of freedom. For these reasons we anticipate that the constraint method may be superior for diatomics.

References

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