Numerical integration of the equations of motion for rigid polyatomics: The matrix method

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A new scheme for numerical integration of motion for classical systems composed of rigid polyatomic molecules is proposed. The scheme is based on a matrix representation of the rotational degrees of freedom. The equations of motion are integrated within the Verlet framework in velocity form. It is shown that, contrary to previous methods, in the approach introduced the rigidity of molecules can be conserved automatically without any additional transformations. A comparison of various techniques with respect to numerical stability is made.

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I. INTRODUCTION

Many approaches in physical chemistry deal with model systems consisting of classical rigid molecules. In studying such systems by the method of molecular dynamics (MD), three problems arise at least: (a) the choice of suitable parameters for describing a state of the system in phase space, (b) the application of an efficient algorithm to integrate numerically the equations of motion, and (c) the exact conservation of the rigidity of molecules during an approximate integration. The question of how best to handle these problems is one which has been keenly debated and the relative merits of a number of various schemes have been devised.

The molecular approach treats dynamics of the system in view of translational and rotational motions. In the classical scheme [1], three Eulerian angles are used to represent the same number of rotational degrees of freedom of the molecule. A numerical integration of the corresponding equations of motion was performed in early investigations [2, 3]. It has been soon established [4, 5] that this integration is very inefficient because of singularities whenever the azimuthal angle of the molecule takes a value of 0 or π. Although the singularities can be avoided by applying different sets of Eulerian angles, this requires complex manipulations with time-consuming trigonometric functions. In singularity free schemes, the orientations of molecules are expressed in terms of either quaternions [6–10] or principal-axis vectors [6]. The last scheme has been derived extending the symmetry vector method [11, 12] for diatomics to an arbitrary rigid body.

In the atomic approach [13], the phase trajectories are considered as translational displacements of individual molecular sites. Such particles move independently under the potential-energy forces and constraint forces, introduced to hold inter-atomic distances constant. This approach is intensively exploited in MD simulations since usual algorithms for integration of translational motion can be applied here. However, the atomic technique is sophisticated to implement for point molecules and when there are more than two, three or four interaction sites in the cases of linear, planar and three-dimensional molecules, respectively, because then the orientations can not be defined uniquely [14]. Moreover, to reproduce exactly the rigid molecular structure for arbitrary polyatomics, it is necessary to solve complicated systems of six nonlinear equations per molecule at each time step of the integration process.
Usually, high-order predictor-corrector algorithms [15, 16] are applied to integrate the equations of rotational motion [2, 7, 8]. Such algorithms, being very accurate at small time steps, quickly become unstable and can not be used for greater step sizes [14]. Small time steps are impractical in calculations, because too much expensive computer time is required to cover the sufficient phase space. At the same time, translational motion is successfully integrated with the lower-order Verlet [17], leapfrog [18], velocity Verlet [19] and Beeman [20] algorithms, owing their simplicity and exceptional numerical stability (for example, the equations of atomic motion are integrated within the usual Verlet framework [13, 14]). However, original versions of these algorithms were constructed on an assumption that acceleration is velocity-independent, and, therefore, they can not be applied directly to rotational dynamics. Analogous pattern arises with translational motion in the presence of external magnetic fields or when relativistic effects are important and it is necessary to take into account internal fields of moving charges.

To remedy that omission, Fincham [21, 22] has proposed explicit and implicit versions of the leapfrog algorithm for rotational motion in which angular momenta are involved into the integration. In the case of a more stable implicit version, this leads to a system of four nonlinear equations per molecule for the same number of quaternion components, which is solved by iteration [22]. Ahlrichs and Brode have derived a hybrid method [23] in which the principal axes are considered as pseudo particles and constraint forces are introduced to maintain their orthonormality. The evolution of principal axes in time can be determined using a recursive solution for exponential propagators. In such a way some difficulties of the cumbersome atomic technique have been obviated. But the algorithm is within the Verlet framework and does not involve angular velocities. Therefore, it is impossible to extend it to a thermostat version or to an integration in the presence of magnetic fields. Moreover, the pseudo-particle formalism does not contain molecular torques, so that it is not so simple matter to apply it to systems with point multipoles. Finally, the recursive method [23] as well as the rotational-motion leapfrog algorithms [22] appear to be much less efficient with respect to the total energy conservation than the atomic-constraint technique.

In the present paper we develop the idea of using principal-axis vectors as orientational variables. We involve the velocities and molecular torques explicitly and show that the
rigidity problem can easily be resolved in our approach without any additional transformations. The paper is organized as follows. The equations of motion for orientational matrices are obtained in Sec. 2. The question of how to integrate these equations within the Verlet framework in velocity form is considered in Sec.3. A comparison of different approaches, based on actual MD simulations of water, is presented in Sec.4. Concluding remarks are added in Sec.5.

II. EQUATIONS OF MOLECULAR MOTION

Let us consider a system composed of $N$ identical rigid molecules with $M$ atoms. We split evolution of the system in time $t$ into translational and rotational motions. The translational motions are applied with respect to the molecule as a whole and can be described by the $3N$ $(i = 1, \ldots, N)$ Newton equations

$$m \frac{d^2 \mathbf{r}_i}{dt^2} = \sum_{j;a,b}^{N,M} \mathbf{F}_{ij}^a_b (|\mathbf{r}_i^a - \mathbf{r}_j^b|) \equiv \mathbf{F}_i(t) ,$$

where $\mathbf{r}_i = \sum_a^M m_a \mathbf{r}_i^a / m$ and $\mathbf{r}_i^a$ are the positions of the centre of mass and atom $a$ of molecule $i$, respectively, $m = \sum_a^M m_a$ and $m_a$ denote the masses of a separate molecule and partial atoms, and $\mathbf{F}_{ij}^a_b$ are the atom-atom forces between two different molecules.

To analyze rotational motions, we introduce the sets $\mathbf{e} \equiv (\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$ and $\mathbf{u}^i \equiv (\mathbf{u}_{1}^i, \mathbf{u}_{2}^i, \mathbf{u}_{3}^i)$ of orthogonal unit vectors characterizing the laboratory fixed coordinate system, L, and the moving coordinate system, $S^i$, attached to molecule $i$, respectively. Orientations of the $S^i$-system with respect to the laboratory frame can be defined as $\mathbf{u}_{\alpha}^i = \sum_\beta a_{\alpha\beta}^i \mathbf{e}_\beta$, or merely $\mathbf{u}^{i+} = \mathbf{A}_i \mathbf{e}^+$, where $\mathbf{e}^+$ and $\mathbf{u}^{i+}$ are vector-columns, $a_{\alpha\beta}^i = \mathbf{u}_{\alpha}^i \cdot \mathbf{e}_\beta$ are components of the rotational matrix $\mathbf{A}_i$ and $\alpha, \beta = 1, 2, 3$. Let us place the origin of the $S^i$-system in the centre of mass of the $i$-th molecule and direct the axes of this system along the principal axes of inertia. The principal components of angular velocities, $\mathbf{\Omega}_i = \Omega_{1}^i \mathbf{u}_1^i + \Omega_{2}^i \mathbf{u}_2^i + \Omega_{3}^i \mathbf{u}_3^i$, obey $3N$ Euler equations [2],

$$J_\alpha \frac{d\Omega_{\alpha}^i}{dt} = K_{\alpha}^i(t) + \left( J_\beta - J_\gamma \right) \Omega_{\beta}^i(t) \Omega_{\gamma}^i(t) ,$$

where $(\alpha, \beta, \gamma) = (1, 2, 3); (2, 3, 1) \text{ and } (3, 1, 2)$. Here $J_1$, $J_2$ and $J_3$ are the independent on time principal moments of inertia of the molecule, $\sum_{j;a,b} \delta_{ij}^a \times \mathbf{F}_{ij}^a = k_1^i \mathbf{e}_1 + k_2^i \mathbf{e}_2 + k_3^i \mathbf{e}_3 =$
$K^+_i u^+_i + K^2_2 u^+_2 + K^3_3 u^+_3$ is the torque exerted on molecule $i$ with respect to its centre of mass due to the interactions with the other molecules, $K_i^+ = A_i k^+_i$, where $K_i = (K^1_i, K^2_i, K^3_i)$, $k_i = (k^1_i, k^2_i, k^3_i)$ and $\delta^a_i = r^a_i - r_i$. Let $\Delta^a = (\Delta^a_1, \Delta^a_2, \Delta^a_3)^+$ be a vector-column of positions for atom $a$ within the molecule in the $S^i$-system, i.e., $\delta^a_i = \Delta^a_1 u^+_1 + \Delta^a_2 u^+_2 + \Delta^a_3 u^+_3$. By construction of the $S^i$-system the conservative set ($a = 1, \ldots, M$) of vectors $\Delta^a$ is the same for each molecule and defined by its rigid geometry. Then the positions of atoms in the $L$-system at time $t$ are $r^a_i(t) = r_i(t) + A^+_i(t) \Delta^a$, where $A^+$ denotes the matrix transposed to $A$.

Usually, the elements of orientational matrices $A_i$ are expressed via three Eulerian angles which can be chosen as follows: $\cos \theta_i = e_3 \cdot u^+_3$, $\cos \varphi_i = e_2 \cdot (e_3 \times u^+_3)/|e_3 \times u^+_3|$ and $\cos \psi_i = u^+_2 \cdot (e_3 \times u^+_3)/|e_3 \times u^+_3|$. Then principal components of angular velocity are $\Omega^1_i = \dot{\theta}_i \sin \psi_i - \dot{\varphi}_i \sin \theta_i \cos \psi_i$, $\Omega^2_i = \dot{\theta}_i \cos \psi_i + \dot{\varphi}_i \sin \theta_i \sin \psi_i$ and $\Omega^3_i = \dot{\varphi}_i \cos \theta_i + \dot{\psi}_i$. As was mentioned earlier, the equations of motion are singular in this case. The most notorious demonstration is the expression $(\Omega^2_i \sin \psi_i - \Omega^1_i \cos \psi_i)/\sin \theta_i$ for the generalized velocity $\dot{\varphi}_i$ from which it follows that $\dot{\varphi}_i \to \infty$ when $\theta_i$ tends to zero or $\pi$. This leads to serious technical disadvantages for the application of Eulerian angles to numerical calculations.

It is worth mentioning that the rigidity of molecules is conserved automatically in this approach, i.e., $|\delta^a_i(t)|^2 = (A^+_i(t) \Delta^a)^+ (A^+_i(t) \Delta^a) = \Delta^a A_i(t) A^+_i(t) \Delta^a = |\Delta^a|^2$, where the property $A A^+ = I$ of rotational matrices has been used and $I$ is the unit matrix. In other words, the matrix $A_i$ remains an orthonormal one for arbitrary values of Eulerian angles.

As is now well established [6, 7], at least four orientational parameters per molecule must be used to avoid the singularities. In this case the matrix $A_i$ is a function of these parameters which constitute the so-called quaternion $q_i \equiv (\xi_i, \eta_i, \zeta_i, \chi_i)$. It is necessary to emphasize that the matrix $A_i$ is orthonormal if the quaternion satisfies the equality $q^2_i = \xi^2_i + \eta^2_i + \zeta^2_i + \chi^2_i = 1$. In practice, however, the equations of motion are not solved exactly, so that this constraint will only be satisfied approximately. The simplest way to achieve the required unit norm at all times lies in multiplying each quaternion component, associated with the same molecule, by the common factor $1/\sqrt{q^2_i}$ at every time step of the numerical integration [7, 22].

In the mentioned above approaches, orientations of the $S^i$-system with respect to the
laboratory frame were defined by the matrix $A_i$, where each of the nine elements $|a^i_{\alpha\beta}| \leq 1$ of which is a function of either three Eulerian angles or four quaternion components. Now involving no Eulerian angles and quaternions, we merely consider all these elements as parameters which represent the rotational degrees of freedom. The elements $a^i_{\alpha\beta}$ are, in fact, the Cartesian coordinates of principal axes of molecules in the laboratory frame. They are not independent as it follows from the requirement $A_iA^+_i = I$ imposed on rotational matrices. For example, the first three elements $a^i_{11}$, $a^i_{12}$ and $a^i_{13}$ can be expressed via the rest of others from the vector relation $u^i_1 = u^i_2 \times u^i_3$, reducing the number of orientational parameters per molecule from 9 to 6. The remaining six elements are connected by three constraints, namely, $u^i_2 \cdot u^i_2 = 1$, $u^i_3 \cdot u^i_3 = 1$ and $u^i_2 \cdot u^i_3 = 0$. Thus, among these six elements we can choose arbitrarily three ones, not belonging the same row of the matrix, to form an independent set, but only with a few exceptions. Indeed, let $a^i_{21}$, $a^i_{22}$ and $a^i_{33}$ be chosen as independent elements and one considers a particular case, when $a^i_{33} = \pm 1$. Then from the equality $u^i_3 \cdot u^i_3 = 1$ it immediately follows that $a^i_{31} = a^i_{32} = 0$. From the next equality $u^i_2 \cdot u^i_3 = 0$ we find that $a^i_{23} = 0$ and, finally, the third relation $u^i_2 \cdot u^i_2 = 1$ yields the constraint $a^i_{21}^2 + a^i_{22}^2 = 1$ concerning the variables which were assumed to be as independent quantities.

The reason of this situation is similar to that existing in the case of using Eulerian angles, where the singularities have appeared at $\theta_i = 0$ or $\pi$, i.e., at $a^i_{33} = \cos \theta_i = \pm 1$. It indicates again about the impossibility to derive singularity free equations of motion involving only three orientational variables per molecule. As was pointed out earlier, four orientational parameters avoid the singularities for arbitrary polyatomic molecules. Nevertheless, a larger number of parameters can also be acceptable, but this leads to an increased number of constraints. For instance, there is one constraint per molecule for quaternion variables, while there are three or even six constraints for six or nine parameters in our case. From this point of view, such an original presentation [6] of the matrix approach has no advantages with respect to the quaternion method. However, as we shall show in the next section using some specific properties of the matrix representation, the constraints can be satisfied intrinsically within particular integration frameworks without any additional transformations.

The equations of motion for dynamical variables $a^i_{\alpha\beta}$ can be found as follows. From
the definition $du^i_\alpha/dt = \Omega_i \times u^i_\alpha$ of angular velocity and the orthonormality of sets $e$ and $u^i$, we obtain $\dot{a}_i^1 = \Omega_2^i a_2^i - \Omega_3^i a_3^i$, $\dot{a}_2^i = \Omega_1^i a_1^i - \Omega_3^i a_1^i$ and $\dot{a}_3^i = \Omega_2^i a_1^i - \Omega_1^i a_2^i$, or in the matrix form

$$\dot{A}_i = \Omega_i A_i ,$$

(3)

where

$$\Omega_i = \begin{pmatrix} 0 & \Omega_3^i & -\Omega_2^i \\ -\Omega_3^i & 0 & \Omega_1^i \\ \Omega_2^i & -\Omega_1^i & 0 \end{pmatrix} ,$$

(4)

are antisymmetric matrices associated with angular velocities $\Omega_i$. Then differentiating relations (3) with respect to time, one obtains the $9N$ ($i = 1, \ldots, N$) scalar equations of motion

$$\ddot{A}_i = \dot{\Omega}_i A_i + \Omega \dot{A}_i = \dot{\Omega}_i A_i + \Omega_i \Omega_i A_i ,$$

(5)

where $\dot{\Omega}_i$ are defined according to Euler equations (2) and angular velocities are excluded from equalities (3), i.e., $\Omega_i = \dot{A}_i A_i^+$. In such a way we construct the coupled set (1), (5) of $12N$ differential equations of type $F(\{ r_i, \dot{r}_i, A_i, \dot{A}_i, \ddot{A}_i \}) = 0$ in terms of the $12N$ generalized coordinates $\{ r_i, A_i \}$. If an initial state $\{ r_i(t_0), \dot{r}_i(t_0), A_i(t_0), \dot{A}_i(t_0) \}$ is specified, the time evolution $\{ r_i(t), A_i(t) \}$ of the system can be unambiguously determined by (1) and (5).

III. INTEGRATION WITHIN THE VELOCITY VERLET FRAMEWORK

The equations of motion obtained must be complemented by an integration algorithm in order to be applicable for actual simulations. As was demonstrated for the atomic approach [13, 14], a very efficient technique follows from the Verlet algorithm. The same framework has been used in the pseudo-particle formalism [23]. However, the Verlet algorithm in its original form [17] does not involve velocity explicitly into the integration process and, therefore, it can not be applied to equations of motion with velocity-dependent accelerations, as in our case (see eq. (5)). Because of this we shall work within a velocity form [19] of the Verlet method.
A. Basic ideas

Let \( \{ \mathbf{r}_i(t_0), \dot{\mathbf{r}}_i(t_0), \mathbf{A}_i(t_0), \dot{\mathbf{A}}_i(t_0) \} \) be a spatially-velocity configuration of the system at time \( t_0 \). On the basis of equations (1) for translational motion we can calculate the translational accelerations \( \ddot{\mathbf{r}}_i(t_0) \) using molecular forces \( \mathbf{F}_i(t_0) \). Then, according to the first line of the velocity Verlet integrator, the positions of the centres of mass of molecules \((i = 1, \ldots, N)\) at time \( t_0 + \Delta t \) are

\[
\mathbf{r}_i(t_0 + \Delta t) = \mathbf{r}_i(t_0) + \dot{\mathbf{r}}_i(t_0) \Delta t + \ddot{\mathbf{r}}_i(t_0) \Delta t^2 / 2 + \mathcal{O}(\Delta t^3),
\]

(6)

where \( \Delta t \) is the time step. Analogously, basing on the equations for rotational motion (2), we define angular accelerations \( \dot{\Omega}_i \) and, therefore, two-fold time derivatives \( \ddot{\mathbf{A}}_i(t_0) \) (5), using principal torques \( \mathbf{K}_i(t_0) \) and taking into account that \( \Omega_i = \dot{\mathbf{A}}_i \mathbf{A}_i^+ \). So that the matrices \( \mathbf{A}_i \) at time \( t_0 + \Delta t \) can be evaluated as follows

\[
\mathbf{A}_i(t_0 + \Delta t) = \mathbf{A}_i(t_0) + \dot{\mathbf{A}}_i(t_0) \Delta t + \ddot{\mathbf{A}}_i(t_0) \Delta t^2 / 2 + \mathcal{O}(\Delta t^3).
\]

(7)

And now we consider how to perform the second line

\[
\dot{s}(t_0 + \Delta t) = \dot{s}(t_0) + \left( \ddot{s}(t_0) + \ddot{s}(t_0 + \Delta t) \right) \Delta t / 2 + \mathcal{O}(\Delta t^3)
\]

(8)

of the velocity Verlet framework, where \( s \) denotes a spatial coordinate. There are no problems to pass this step in the case of translational motion, when \( \dot{s} \equiv \dot{r}_i \) and, therefore, for new translational velocities one obtains

\[
\dot{r}_i(t_0 + \Delta t) = \dot{r}_i(t_0) + \left( \ddot{r}_i(t_0) + \ddot{r}_i(t_0 + \Delta t) \right) \Delta t / 2 + \mathcal{O}(\Delta t^3),
\]

(9)

where \( \ddot{r}_i(t_0 + \Delta t) = \frac{1}{m} \mathbf{F}_i(t_0 + \Delta t) \) and the forces \( \mathbf{F}_i(t_0 + \Delta t) \) are calculated in the already defined new spatial configuration \( \{ \mathbf{r}_i(t_0 + \Delta t), \mathbf{A}_i(t_0 + \Delta t) \} \).

However, the difficulties immediately appear in the case of rotational dynamics, because then second time derivatives \( \ddot{s} \) can depend explicitly not only on spatial coordinates \( s \), associated with the rotational degrees of freedom, but also on generalized velocities \( \dot{s} \). For example, according to Euler equations (2), the principal angular accelerations depend on orientational variables via molecular torques and on angular velocities of molecules as
well. Then, choosing $s \equiv A_i$, we obtain on the basis of the equations of motion (5) that
\[ \ddot{A}_i(t) \equiv \ddot{A}_i(A_i(t), \dot{A}_i(t)) \]
In view of (8), this leads to a very complicated system of nine nonlinear equations per molecule with respect to the nine unknown elements of matrix $\dot{A}_i(t+\Delta t)$. It is worth to note that similar problems arise within the leapfrog and Beeman frameworks (see Appendix, where a rotational-motion version of the Beeman algorithm is derived).

An alternative has been found in rotational-motion versions [21, 22] of the leapfrog algorithm. It has been assumed to associate the quantity $\dot{s}$ with the angular momentum $l_i = A_i^\dagger L_i$ of the molecule in the laboratory system of coordinates, i.e., $\dot{s} \equiv l_i$, where $L_i = (J_1 \Omega_1^i, J_2 \Omega_2^i, J_3 \Omega_3^i) = J_i \Omega_i$ and $J$ is the diagonal matrix of principal moments of inertia. The rate of change in time of angular momentum is the torque, i.e., $\dot{l}_i = k_i$. Then equation (8) leads to a much more simple expression,

$$ l_i(t_0 + \Delta t) = l_i(t_0) + \left( k_i(t_0) + k_i(t_0 + \Delta t) \right) \Delta t/2 + \mathcal{O}(\Delta t^3), $$

(10)

and, therefore, new angular momenta are easily evaluated using the known torques $k_i$ at times $t_0$ and $t_0 + \Delta t$. The corresponding values for principal angular velocities and first time derivatives of orientational matrices can be obtained, when they are needed, using the relations $\dot{\Omega}_i(t_0 + \Delta t) = J_i^{-1} A_i(t_0 + \Delta t) l_i(t_0 + \Delta t)$ and $\dot{\dot{A}}_i(t_0 + \Delta t) = \dot{\Omega}_i(t_0 + \Delta t) A_i(t_0 + \Delta t)$.

Finally, we consider the third version of the velocity Verlet method. The idea consists in using angular velocities as independent parameters for describing the state of the system in phase space. Then putting $s \equiv \Omega_i$ in (8) and taking into account Euler equations (2), we find the following result

$$ \Delta \Omega_i^\alpha = \frac{\Delta t}{2 \omega_\alpha} \left[ K_\alpha^\beta(t) + K_\alpha^\beta(t_0 + \Delta t) + \left( J_\beta - J_\gamma \right) \right] \times \left( 2 \Omega_\beta(t_0) \omega_\beta^\alpha(t_0) + \Omega_\beta(t_0) \Delta \Omega_\gamma^\alpha + \Omega_\gamma(t_0) \Delta \Omega_\beta^\alpha + \Delta \Omega_\beta^\alpha \Delta \Omega_\gamma^\alpha \right), $$

(11)

The equations (11) constitute the system of maximum three nonlinear equations per molecule with respect to the same number of the unknowns $\Delta \Omega_i^\alpha = \Omega_i^\alpha(t_0 + \Delta t) - \Omega_i^\alpha(t_0)$. The system (11) can be linearized, substituting initially $\Delta \Omega_i^\alpha = 0$ in all quadratic terms, and solved in a quite efficient way by iteration. This is justified for $\Delta t \to 0$ because then terms nonlinear in $\Delta \Omega_i^\alpha$ are small.
From the mathematical point of view, all the three representations \( \dot{s} \equiv \dot{A}_i, l_i, \) or \( \Omega_i \) are completely equivalent, because the knowledge of an arbitrary quantity from the set \( (\dot{A}_i, l_i, \Omega_i) \) allows us to determine the rest of two ones uniquely. In the case of numerical integration the pattern is different, because then the investigated quantities are evaluated approximately. The choice \( \dot{s} \equiv \dot{A}_i \) can not be recommended for calculations due to its complexity. The case of \( \dot{s} \equiv l_i \), corresponding to the angular-momentum version of the Verlet algorithm, is the most attractive in view of the avoidance of nonlinear equations. Actual computations show, however, that the best numerical stability with respect to the total energy conservation is reached in the angular-velocity version (11) of the Verlet algorithm, when \( \dot{s} \equiv \Omega_i \). This fact can be explained taking into account that a kinetic part, \( \frac{1}{2} \sum_{i=1}^{N} (J_1\Omega_1^2 + J_2\Omega_2^2 + J_3\Omega_3^2) \), of the total energy is calculated directly from principal angular velocities. At the same time, to evaluate angular velocities within the angular-momentum version the additional transformations \( \Omega_i = J^{-1}A_i l_i \) with approximately computed matrices \( A_i \) and angular momenta \( l_i \) are necessary. They contribute additional portions into the accumulated errors at calculations of the total energy.

Shifting the initial time \( t_0 \) to \( t_0 + \Delta t \), the integration process is repeated for a next time step. In such a way, step by step the dynamics of the system can be evaluated.

B. Solving the rigidity problem

Let us write an analytical solution for orientational matrices in the form

\[
A_i(t_0 + \Delta t) = \sum_{p=0}^{P} A_i^{(p)}(t_0) \frac{\Delta t^p}{p!} + \mathcal{O}(\Delta t^{P+1}), \tag{12}
\]

where \( A_i^{(p)}(t_0) \) denotes the \( p \)-fold time derivative of \( A_i \) at time \( t_0 \). It can be shown easily from the structure of equation (3) that arbitrary-order time derivatives of the matrix constraint \( \Theta_i(t) \equiv A_i(t)A_i^+(t) - I = 0 \) are equal to zero at a given moment of time, i.e.,

\[
\dot{A}_i A_i^+ + A_i \dot{A}_i^+ = 0, \quad \ddot{A}_i A_i^+ + 2\dot{A}_i \dot{A}_i^+ + A_i \ddot{A}_i^+ = 0
\]

and so on, when \( A_i \) is orthonormal. Therefore, if all the terms \( (P \to \infty) \) of Taylor’s expansion (12) are taken into account, that corresponds to the exact solution of equations of motion, and initially all the constraints are satisfied, \( \Theta_i(t_0) = 0 \), they will be fulfilled at later times as well.

In particular algorithms the expansion is truncated after a finite number of terms.
For example, the velocity-Verlet form (7) is restricted by quadratic terms \( P = 2 \), involving truncation errors of order \( \Delta t^3 \) into the matrix elements of \( A_i \). The same order of uncertainties will be accumulated in \( \Theta_i(t) \) at each time step, breaking the molecular structure, i.e., \( \Theta_i(t_0 + \Delta t) = O(\Delta t^3) \). In such a case the molecules collapse and can even be destroyed completely after a sufficient period of time. Therefore, the problem arises: how to modify the first line of the algorithm to achieve the exact rigidity for arbitrary times?

1. **Constraint-matrix scheme**

   The usual way to reduce orientational matrices to orthonormal form lies in using the constraint technique. The main idea is simple. As far as the elements of orientational matrices are not independent, this requires, generally speaking, the necessity of introducing additional forces which appear as a result of the constraints \( \Theta_i(t) = 0 \). These matrix constraints constitute, in fact, six independent scalar relations per molecule, namely,

   \[
   \begin{align*}
   \phi_1^i & \equiv a_{11}^i + a_{12}^i + a_{13}^i - 1 = 0 , \\
   \phi_2^i & \equiv a_{21}^i + a_{22}^i + a_{23}^i - 1 = 0 , \\
   \phi_3^i & \equiv a_{31}^i + a_{32}^i + a_{33}^i - 1 = 0 , \\
   \phi_4^i & \equiv a_{11}^i a_{22}^i + a_{12}^i a_{21}^i + a_{13}^i a_{23}^i = 0 , \\
   \phi_5^i & \equiv a_{11}^i a_{31}^i + a_{12}^i a_{32}^i + a_{13}^i a_{33}^i = 0 , \\
   \phi_6^i & \equiv a_{21}^i a_{31}^i + a_{22}^i a_{32}^i + a_{23}^i a_{33}^i = 0 .
   \end{align*}
   \]

Then the corresponding constraint forces, acting on dynamical variables \( a_{\alpha\beta}^i \), are \( G_{\alpha\beta}^i = -\sum_{l=1}^6 \lambda_l \partial \phi_l^i / \partial a_{\alpha\beta}^i \) or in the matrix representation

\[
G_i = -\Lambda_i A_i \equiv - \begin{pmatrix} 2\lambda_1^i & \lambda_4^i & \lambda_5^i \\ \lambda_4^i & 2\lambda_2^i & \lambda_6^i \\ \lambda_5^i & \lambda_6^i & 2\lambda_3^i \end{pmatrix} A_i ,
\]

where \( \Lambda_i \) are symmetric matrices of Lagrange multipliers. The matrices of constraint forces are now added in the equations of motion (5) and, as a consequence, the evaluation of matrix elements (7) is modified to

\[
A_i(t_0 + \Delta t) = A_i(t_0) + \dot{A}_i(t_0) \Delta t + \ddot{A}_i(t_0) \Delta t^2 / 2 + G_i(t_0) \Delta t^2 / 2 + O(\Delta t^3) .
\]

In view of equations (14) and (15), to satisfy the conditions \( \Theta_i(t_0 + \Delta t) = 0 \) it is necessary to solve the system \( \phi_l^i(t_0 + \Delta t) = 0 \) of six \( (l = 1, \ldots, 6) \) nonlinear equations
per molecule for six unknown Lagrange multipliers \( \lambda^i(t_0) \). As usually, such a system is linearized and the unknowns are found by iteration. The iteration procedure can be initiated by putting \( \lambda^i = 0 \) in all nonlinear terms and the iterations converge rapidly at actual step sizes to the physical solutions \( \lambda^i(t_0) \sim \Delta t \). The contributions of constraint forces into the matrix evaluation (15) are of order \( \Delta t^3 \), i.e., the same order as truncation errors of the basic algorithm (7), but the rigidity is now fulfilled perfectly for arbitrary times in future. It is worth to remark that the constraint forces introduced should be treated as pseudo forces, because they depend on details of the numerical integration in a characteristic way and disappear if the equations of motion are solved exactly, i.e., when \( \Delta t \to 0 \).

2. Rotational-matrix scheme

Fortunately, the cumbersome procedure of solving nonlinear equations to preserve the molecular rigidity can be avoided in our approach using the fact that actual algorithms are accurate to a finite order only in time step. In view of equalities (3) and (5), the evaluation (7) can be presented in a more compact form,

\[
A_i(t_0 + \Delta t) = D_i(t_0, \Delta t)A_i(t_0) + \mathcal{O}(\Delta t^3),
\]

where

\[
D_i(t_0, \Delta t) = I + \Omega_i(t_0)\Delta t + \left( \dot{\Omega}_i(t_0) + \Omega_i^2(t_0) \right) \Delta t^2/2
\]

are evolution matrices. Let the rigidity has been satisfied at time \( t_0 \), i.e., \( \Theta_i(t_0) = A_i(t_0)A_i^+(t_0) - I = 0 \). Then \( \Theta_i(t_0 + \Delta t) = D_i(t_0, \Delta t)D_i^+(t_0, \Delta t) - I = \mathcal{O}(\Delta t^3) \) or, in other words, the matrices \( D_i \) are not orthonormal.

The simplest way to present the evolution matrices and, as a consequence, the orientational matrices in orthonormal form lies in the following. Taking into account that \( \Omega_i^2 = W(\Omega_i) - \Omega_i^2I \), where \( \Omega_i = \sqrt{\Omega_1^2 + \Omega_2^2 + \Omega_3^2} \) is the magnitude of the angular velocity and \( W(\Omega_i) \) is a symmetric matrix with the elements \( \Omega^i_{\alpha}\Omega^j_{\beta} \), we rewrite (17) as

\[
D_i(t_0, \Delta t) = (1 - \Omega_i^2(t_0)\Delta t^2/2)I + W_i(\Omega_i(t_0))\Delta t^2/2 + \overline{\Omega}_i(t_0)\Delta t,
\]
where $\mathbf{\Pi}_i(t_0)$ is an antisymmetric matrix of type (4), constructed on the mean value $\mathbf{\Pi}_i(t_0) = \mathbf{\Omega}_i(t_0) + \dot{\mathbf{\Omega}}_i(t_0) \Delta t/2$ of the angular velocity for the $i$-th molecule during the time interval $[t_0, t_0 + \Delta t]$. It is easy to see that replacing $\mathbf{\Omega}_i$ by $\mathbf{\Pi}_i$ in (18), we introduce the error of order $\Delta t^3$. Moreover, taking into account that

$$\Delta t = \frac{\sin(\mathbf{\Pi}_i \Delta t)}{\mathbf{\Pi}_i} + O(\Delta t^3), \quad \frac{\Delta t^2}{2} = 1 - \frac{\cos(\mathbf{\Pi}_i \Delta t)}{\mathbf{\Pi}_i^2} + O(\Delta t^4),$$

we adjust (18) to the form

$$\mathbf{D}_i(t_0, \Delta t) = I \cos(\mathbf{\Pi}_i \Delta t) + \frac{1 - \cos(\mathbf{\Pi}_i \Delta t)}{\mathbf{\Pi}_i^2} \mathbf{W}(\mathbf{\Pi}_i) + \frac{\sin(\mathbf{\Pi}_i \Delta t)}{\mathbf{\Pi}_i} \mathbf{\Pi}_i \equiv \exp(\mathbf{\Pi}_i(t_0) \Delta t).$$

(20)

Let us expand the matrix $\mathbf{D}_i(t_0, \Delta t)$ into the Taylor’s series with respect to $\Delta t$. Then it can be verified easily that each elements of this matrix coincides with the corresponding element of $\mathbf{D}_i(t_0, \Delta t)$ (17) up to the second order in $\Delta t$ inclusively. Higher order terms, being associated with time derivatives of angular accelerations, are not taken into account within the velocity Verlet framework and they can merely be omitted without loss of the precision. Therefore, the matrices $\mathbf{D}_i(t_0, \Delta t)$ (20) and $\mathbf{D}_i(t_0, \Delta t)$ (17) differ between themselves by terms of order $\Delta t^3$ or higher that is completely in the self-consistency with truncation errors of the algorithm considered. However, the main advantage of using $\mathbf{D}_i$, instead of $\mathbf{D}_i$, in the evaluation

$$\mathbf{A}_i(t_0 + \Delta t) = \mathbf{D}_i(t_0, \Delta t) \mathbf{A}_i(t_0) + O(\Delta t^3),$$

(21)

of orientational variables consists in the fact that the matrix $\mathbf{D}_i(t_0, \Delta t)$ is orthonormal, i.e., $\mathbf{D}_i(t_0, \Delta t) \mathbf{D}_i^+(t_0, \Delta t) = I$ and then $\mathbf{\Theta}_i(t_0 + \Delta t) = \mathbf{D}_i(t_0, \Delta t) \mathbf{D}_i^+(t_0, \Delta t) - I = 0$. As it follows from the structure of eq. (20), the matrix $\mathbf{D}_i(t_0, \Delta t)$ defines the three-dimensional rotation on angle $\mathbf{\Pi}_i \Delta t$ around the axis directed along vector $\mathbf{\Pi}_i$. In such a way, the rigid structures of molecules can be reproduced exactly at each time step of the integration.

IV. NUMERICAL TESTS AND DISCUSSION

We now test our matrix method on the basis of simulations on a TIP4P model [24] of water. This method was used by us previously [25] investigating a Stockmayer
fluid of point dipoles. In the TIP4P model the water molecule consists of four sites, $M = 4$. We have used a system of $N = 256$ molecules and the interaction site reaction field geometry [26]. Intersite components of the TIP4P potential were cut off and shifted to zero at point of the truncation to avoid the system energy drift associated with the passage of the sites through the surface of the cut-off sphere. The cut-off radius was half the basic cell length. The MD simulations were performed in the microcanonical ensemble at a density of 1 g/cm$^3$ and at a temperature of 298 K. The numerical stability of solutions to the equations of motion was identified in terms of relative fluctuations, 

$$
\mathcal{E}(t) = \sqrt{\langle (E - \langle E \rangle_t)^2 \rangle_t / \langle E \rangle_t^2},
$$

of the total energy $E$ of the system during time $t$.

We have made a comparative test carrying out explicit MD runs using our angular-velocity Verlet integrator (eq. (11)) within constraint- and rotational-matrix schemes (eqs. (15) and (21), respectively), as well as the implicit quaternion leapfrog algorithm [22], the pseudo-particle formalism [23] and the atomic-constraint technique [13]. The runs were started from an identical well equilibrated configuration. All the algorithms required almost the same computer time per step (96% being spent to evaluate pair interactions). For the purpose of comparison the quaternion integration with the Gear predictor-corrector algorithm of fifth order [15, 16] has been considered as well. At least two corrector steps were used to provide an optimal performance of the predictor-corrector scheme and, as a consequence, twice or more larger computer time was taken in this case than that is normally necessary.

The results obtained for relative total energy fluctuations as functions of the length of the simulations at four fixed step sizes, $\Delta t = 1, 2, 3$ and 4 fs, are presented in fig. 1 (water is most commonly simulated with a step size of order 2 fs [27]). At small time steps, $\Delta t \leq 1$ fs, all the approaches exhibited similar equivalence in the energy conservation (subset (a) of fig. 1), except the Gear algorithm which produced much more accurate trajectories. But the Gear algorithm begins to be unstable already at $\Delta t = 1$ fs and leads to the worst results for $\Delta t \geq 1.5$ fs (see, as an example, the case $\Delta t = 2$ fs, subset (b)). Somewhat better stability is observed in the leapfrog and pseudo-particle approaches. However, at moderate and great time steps, $\Delta t \geq 2$ fs (figs. 1 (b)–(d)), the results are rather poor, especially in the case of the leapfrog scheme. The best numerical stability has been achieved with the atomic-constraint algorithm and our matrix method, which
conserve the total energy approximately with the same accuracy up to $\Delta t = 3$ fs. It can be seen easily that the matrix method works better within the rotational-matrix scheme, so that there is no need to use the complicated constraint-matrix procedure. Quite a few iterations (the mean number of iterations per molecule varied from 3 to 5 at $\Delta t = 1 \div 4$ fs) was sufficient to obtain solutions to the system of quadratic equations (11) with a relative iteration precision of $10^{-12}$. This contributes a negligible small portion additionally into the total computer time.

To demonstrate that the exact reproduction of molecular rigidity is so important, we have also integrated the equations of motion in a situation (eq. (7)) when no additional normalization and orthogonalization of principal-axis vectors are used. In this case the total energy fluctuations increased drastically with increasing the length of the runs at arbitrary time steps (see, for instance, the corresponding curve in fig. 1 (a)). The same words can be said in the case when no quaternion renormalization is applied along the leapfrog trajectories. This is so because in the free-normalization regime, the structure of molecules is broken that leads to an unpredictable discrepancy in the calculation of potential forces and significant deviations of the total energy. We have also established that the numerical stability is very sensitive to the way of how the quaternion renormalization is performed. In particular, the energy conservation can be somewhat improved if the quaternions are renormalized inside the iterative loop of the implicit leapfrog integrator rather than at the end of each time step only, as was originally proposed [22].

No shift of the total energy has been observed for the atomic-constraint and matrix approaches over a length of 10 ps at $\Delta t \leq 3$ fs. Instead, it oscillates around a stable value of $E_0 = -33.6$ kJ/mol. To reproduce the features of microcanonical ensembles quantitatively, it is necessary for the ratio $\Gamma = \mathcal{E}/\Upsilon$ of total energy fluctuations to fluctuations $\Upsilon$ of the potential energy to be no more than a few per cent. For the system under consideration $\Upsilon \approx 0.56\%$, so that, for example, the level $\mathcal{E} = 0.03\%$ will correspond to $\Gamma \sim 5\%$ that is still acceptable for precision calculations. The ratios $\Gamma$, obtained within various approaches at the end of 10 ps runs, are plotted in fig. 2 as dependent on the time increment. The results of fig. 2 show that a level of $\Gamma = 5\%$ is achieved at the time steps 1.2, 1.4, 3.0 and 4.0 fs within the leapfrog, pseudo-particle, matrix and atomic approaches, respectively. Therefore, the last two methods allow a step size more
than twice larger than the pseudo-particle and leapfrog algorithms. The functions $\Gamma(\Delta t)$ can be interpolated with a great accuracy as $C \Delta t^2 + C' \Delta t^3$ with the coefficients $C \approx 0.28$ and $0.30 \% \text{fs}^{-2}$, $C' \approx 0.01$ and $0.10 \% \text{fs}^{-3}$ for the atomic and matrix approaches, respectively. The characteristic square growth of $\Gamma$ at small time steps is completely in line with $O(\Delta t^2)$ order of global errors for the algorithm considered.

It is worth to underline that analyzing the system over a significantly shorter time period, of order 1 ps say (as was done by Ahlrichs and Brode [23]), one may come to a very misleading idea about the energy conservation. We can see clearly from fig. 1 that such a simulation period (corresponding to 1000, 500, 333 and 250 time steps at $\Delta t = 1, 2, 3$ and 4 fs, respectively) is quite insufficient to give a realistic pattern on global errors accumulated in the total energy. And only beginning from lengths of order 10 ps, we are entitled to formulate true conclusions on the numerical stability. These lengths are sufficiently long to observe an appreciable modification of the system. For instance, during 10 ps even long-lived dipole moment correlations vanish completely [28]. Moreover, the phase trajectories of 10 ps long are also sufficient, as a rule, to reproduce thermodynamic, structure and other properties of water with a reliable statistical accuracy. The investigation of some collective effects, such as dielectric relaxation, may require extremely long simulations (up to 1000 ps [28]) to reduce statistical noise. As a result, even the best algorithms may not provide a required numerical stability. In such a situation, we can merely slightly rescale the velocities of particles when the total energy has exceeded an allowed level. Obviously, the investigated quantities will be little affected by this rescaling if it is applied not more frequently than after a period of time during which the correlations have significantly decayed.

In view of the results obtained in this section, we can conclude that the method proposed appears to be the most efficient among all known algorithms deriving within the molecular framework and can be considered as a good alternative to the cumbersome atomic technique. The fact that our molecular Verlet algorithm conserves the total energy at great step sizes somewhat worse than the atomic Verlet algorithm results from the introduction of velocities. As far as velocities appear explicitly, the angular accelerations begin to be velocity dependent. Further, the angular velocities are calculated with one step errors of order $O(\Delta t^3)$ and the same order of uncertainties will be presented simultaneously.
in angular accelerations. This, in its turn (see eq. (11)), leads to additional terms of orders $O(\Delta t^4)$ and $O(\Delta t^3)$ in the truncation and global errors, respectively, for angular velocities and, as a consequence, for the total energy. That is why in the case of rotational motion the coefficient $C'$ corresponding to the velocity Verlet differs significantly from that obtained for the usual (free of velocities) Verlet algorithm. At the same time, the corresponding values of $C$ are practically equal between themselves, and, therefore, we may stay about the equivalence of the both algorithms with respect to the main term of global errors.

The pointed out above minor disadvantage is compensated, however, by a much more major advantage of our method with respect to the atomic scheme in that the velocity Verlet algorithm allows to perform simulations in canonical ensembles. As is well known [22], thermostat calculations can be carried out with significantly greater step sizes than those used in microcanonical ensembles. A thermostat version of the velocity Verlet algorithm for rotational motion will be studied in a separate investigation.

V. CONCLUSION

We have shown that the difficulties in numerical integration of rigid polyatomics can be overcame using an alternative approach. In our singularity free scheme, orientational matrices were used to represent the rotational degrees of freedom of the system. Although this introduces extra equations per molecule and the lack of independence for the matrix elements, but presents no numerical difficulties. An elegant procedure, built directly into the Verlet algorithm, has allowed to perfectly fulfil the rigidity of molecules at each step of the trajectory without any additional efforts and loss of precision. Avoidance of the necessity to solve complex nonlinear equations for preservation of the molecular rigidity should be a benefit of the matrix method with respect to the atomic-constraint approach.

We have demonstrated on the basis of actual calculations that the matrix method leads to results comparable in efficiency with the cumbersome atomic-constraint technique. The advantages of the matrix scheme are that it can be implemented for arbitrary rigid bodies, extended to a thermostat version and realized in MD programmes in a more simple way.

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Appendix

We now consider the question of how to adopt our matrix scheme to integrate the equations of motion within the Beeman framework. According to the usual Beeman algorithm [20], the translational positions and velocities of molecules are evaluated as

\[
\mathbf{r}_i(t_0 + \Delta t) = \mathbf{r}_i(t_0) + \dot{\mathbf{r}}_i(t_0) \Delta t + \left[ \frac{2}{3} \ddot{\mathbf{r}}_i(t_0) - \frac{1}{6} \dddot{\mathbf{r}}_i(t_0 - \Delta t) \right] \Delta t^2 + O(\Delta t^4),
\]

\[
\ddot{\mathbf{r}}_i(t_0 + \Delta t) = \ddot{\mathbf{r}}_i(t_0) + \left[ \frac{1}{3} \dddot{\mathbf{r}}_i(t_0 + \Delta t) + \frac{2}{6} \dddot{\mathbf{r}}_i(t_0) - \frac{1}{6} \dddot{\mathbf{r}}_i(t_0 - \Delta t) \right] \Delta t + O(\Delta t^3).
\]

(A1)

The order of truncation errors in coordinates increases to four because the expression \([\frac{2}{3} \dddot{\mathbf{r}}_i(t_0) - \frac{1}{6} \dddot{\mathbf{r}}_i(t_0 - \Delta t)] \Delta t^2\) can be reduced to the form \([\dddot{\mathbf{r}}_i(t_0) \Delta t^2/2 + \dddot{\mathbf{r}}_i(t_0) \Delta t^3/6 + O(\Delta t^4)\) with the estimation \(\dddot{\mathbf{r}}_i(t_0) = [\dddot{\mathbf{r}}_i(t_0) - \dddot{\mathbf{r}}_i(t_0 - \Delta t)]/\Delta t + O(\Delta t)\) of superaccelerations. The fractions in the second line of eq. (A1) are obtained in such a way to provide the third order of truncation errors in velocities and to satisfy exactly the Störmer central difference approximation [16, 29] of accelerations

\[
s(t_0 + \Delta t) = -s(t_0 - \Delta t) + 2s(t_0) + \ddot{s}(t_0) \Delta t^2 + O(\Delta t^4)
\]

(A2)

with \(s \equiv \mathbf{r}_i\). Acting in the spirit of the Beeman framework, we can write analogous to (A1) equations for orientational matrices and angular velocities. The result is

\[
\mathbf{A}_i(t_0 + \Delta t) = \mathbf{A}_i(t_0) + \dot{\mathbf{A}}_i(t_0) \Delta t + \left[ \frac{2}{3} \ddot{\mathbf{A}}_i(t_0) - \frac{1}{6} \dddot{\mathbf{A}}_i(t_0 - \Delta t) \right] \Delta t^2
\]

\[
-\left[ \frac{2}{3} \mathbf{A}_i(t_0) \dot{\mathbf{A}}_i(t_0) - \frac{1}{6} \mathbf{A}_i(t_0 - \Delta t) \dot{\mathbf{A}}_i(t_0 - \Delta t) \right] \Delta t^2 + O(\Delta t^4),
\]

(A3)

\[
\Omega_\alpha^{(n+1)}(t_0 + \Delta t) = \Omega_\alpha^{(n)}(t_0) + \frac{\Delta t}{J_\alpha} \left[ \frac{1}{3} \mathbf{K}_\alpha^i(t_0 + \Delta t) + \frac{2}{6} \mathbf{K}_\alpha^i(t) - \frac{1}{6} \mathbf{K}_\alpha^i(t_0 - \Delta t) \right]
\]

\[
	imes \left[ \frac{1}{3} \Omega_\beta^{(n)}(t_0 + \Delta t) \Omega_\gamma^{(n)}(t_0 + \Delta t) + \frac{2}{6} \Omega_\beta^{(n)}(t_0) \Omega_\gamma^{(n)}(t_0 - \Delta t) - \frac{1}{6} \Omega_\beta^{(n)}(t_0 - \Delta t) \Omega_\gamma^{(n)}(t_0 - \Delta t) \right].
\]

(A4)

where the symmetric constraint matrices \(\mathbf{A}_i(t_0) \sim \Delta t^2\) are found from the constraint relations \(\mathbf{A}_i(t_0 + \Delta t) \mathbf{A}_i^+(t_0 + \Delta t) = \mathbf{I}\), whereas new values \(\Omega_\alpha^{(n)}(t_0 + \Delta t)\) for principal components of the angular velocities can be computed by iteration \((n = 0, 1, \ldots)\) taking \(\Omega_\alpha^{(0)}(t_0 + \Delta t) = \Omega_\alpha^i(t_0)\) as initial guesses.

A rotational-matrix scheme can be derived within the Beeman method as follows. Consider first a more general procedure for the orthonormalization of orientational matrices, which will be valid for integrators of arbitrary order in truncation errors. Let the algorithm applied uses
Taylor’s expansion (12) for the time evaluation of orientational matrices. Then the evolution matrices can be cast as

\[ D_i(t_0, \Delta t) = I + \sum_{p=1}^{P} D_i^{(p)}(t_0) \frac{\Delta \Omega^p}{p!}, \quad (A5) \]

where \( D_i^{(p)} = A_i^{(p)} A_i^{+} \), or more explicitly: \( D_i^{(1)} = \Omega_i \), \( D_i^{(2)} = \hat{\Omega}_i + \Omega_i^2 \), \( D_i^{(3)} = \hat{\Omega}_i + 2\hat{\Omega}_i \Omega_i + \Omega_i \hat{\Omega}_i + \Omega_i^3 \), \( D_i^{(4)} = \hat{\Omega}_i + 3\hat{\Omega}_i \Omega_i + \Omega_i \hat{\Omega}_i + 3\Omega_i \hat{\Omega}_i + 2\Omega_i \hat{\Omega}_i \Omega_i + \Omega_i^2 \hat{\Omega}_i + \hat{\Omega}_i^4 \), and so on.

A rotational-matrix counterpart of (A5) we find in the orthonormal form

\[ \mathcal{D}_i(t_0, \Delta t) = \exp \left( \sum_{p=1}^{P} H_i^{(p)}(t_0) \frac{\Delta \Omega^p}{p!} \right), \quad (A6) \]

where \( H_i^{(p)} \) are unknown antisymmetric matrices, i.e., \( H_i^{(p)} = -H_i^{(p)} \), and expand the exponent (A6) into the Taylor series at \( \Delta t \to 0 \). It is obvious that \( D_i(t_0, \Delta t) \) and \( \mathcal{D}_i(t_0, \Delta t) \) will be identical at \( P \to \infty \), if all their matrix coefficients, corresponding to the same powers \( p = 1, 2, \ldots, P \) of \( \Delta t \), are equal between themselves. This condition leads to a recursive procedure with the solutions \( H_i^{(1)} = \Omega_i \), \( H_i^{(2)} = \hat{\Omega}_i \), \( H_i^{(3)} = \hat{\Omega}_i + \frac{1}{2} (\hat{\Omega}_i \Omega_i - \Omega_i \hat{\Omega}_i) \), \( H_i^{(4)} = \hat{\Omega}_i + \hat{\Omega}_i \Omega_i - \hat{\Omega}_i \Omega_i \) and so on. The Beeman approach is accurate to third order in coordinates (\( P = 3 \)), i.e.,

\[ \left[ \frac{\hat{\Omega}}{6} \hat{\Omega}_i(t_0) - \frac{1}{6} \hat{\Omega}_i(t_0 - \Delta t) \right] \Delta t^2 = \hat{\Omega}_i(t_0) \Delta t^2 / 2 + \hat{\Omega}_i(t_0) \Delta t^3 / 6 + O(\Delta t^4), \]

where the superaccelerations \( \hat{\Omega}_i(t_0) = [\hat{\Omega}_i(t_0) - \hat{\Omega}_i(t_0 - \Delta t)] / \Delta t + O(\Delta t) \). Similarly we can estimate angular superaccelerations, \( \hat{\Omega}_i(t_0) = [\hat{\Omega}_i(t_0) - \hat{\Omega}_i(t_0 - \Delta t)] / \Delta t \), and obtain in this case

\[ \mathcal{D}^B_i(t_0, \Delta t) = \exp \left( \Omega_i(t_0) \Delta t + \left[ \frac{\hat{\Omega}_i(t_0)}{3} - \frac{1}{6} \hat{\Omega}_i(t_0 - \Delta t) \right] \Delta t^2 + \left[ \hat{\Omega}_i(t_0) \Omega_i(t_0) - \Omega_i(t_0) \hat{\Omega}_i(t_0) \right] \Delta t^3 \right). \quad (A7) \]

Putting \( P = 2 \) in eq. (A6) yields the result \( \mathcal{D}_i(t_0, \Delta t) = \exp(\Omega_i(t_0) \Delta t + \frac{1}{2} \hat{\Omega}_i(t_0) \Delta t^2) \). As was expected, this is completely in line with the result (20) performed in Sec.3 for the velocity Verlet algorithm on the basis of intuitive grounds.

It is worth mentioning that approximation (A2) is used directly for evaluation of spatial coordinates in the usual Verlet algorithm [17, 23]. As can be verified, any trajectory produced by the velocity Verlet algorithm satisfies equation (A2) at \( s = \{ r_i, A_i \} \) even if constraint- or rotational-matrix schemes are used. The fact that the trajectory \( s(t) \) can be generated with the same fourth-order local errors by lower-order equations (6) and (7) (or (21)) results from a fortunate cancellation of truncation errors arising in coordinates and velocities during two neighbour time steps. Note, however, that the usual Verlet algorithm, its velocity version and Beeman method are not equivalent, because they differ between themselves by the main
term of fourth-order uncertainties in coordinates and calculate one-step velocities in a different manner. For example, evaluating velocities within the Beeman algorithm, it is assumed that the accelerations are slow variables on time scales of $2\Delta t$. If this criterion is not satisfied, the main term $O(\Delta t^3)$ of truncation uncertainties in velocities and, as a result, the main coefficient $C$ in global errors for the total energy may increase in a characteristic way. This prediction has been confirmed by our computer simulations on the TIP4P water. Therefore, the Beeman algorithm can be applied for systems with sufficiently smooth interparticle potentials only.

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Figure captions

**Fig. 1.** The relative total energy fluctuations as functions of the length of the simulations on the TIP4P water, obtained within various techniques at four fixed time steps, namely, 1 fs (a), 2 fs (b), 3 fs (c) and 4 fs (d).

**Fig. 2.** The ratios of the total energy and potential energy fluctuations as dependent on the step size, observed for various approaches in the simulations of the TIP4P water at the end of 10 ps runs.
Fig. 1. I.P. Omelyan

Numerical integration of the equations of motion for rigid polyatomics: The matrix method
Fig. 2. I.P. Omelyan

Numerical integration of the equations of motion for rigid polyatomics: The matrix method