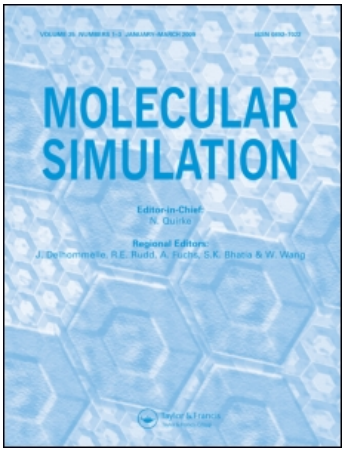

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NEW RIGID BODY EQUATIONS OF MOTION FOR MOLECULAR DYNAMICS

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We derive new constrained equations of motion for the principal axis vectors of a rotating rigid body. The equations of motion in both Lagrangian and Hamiltonian form are derived and, for a simple example, are shown to be equivalent to equations obtained using generalized coordinates. Methods for correcting numerical instabilities are given and the method is illustrated for two small scale simulations of a model for propane.

KEY WORDS: Rigid body, rotation, lagrangian, hamiltonian, molecular dynamics

1 INTRODUCTIONS

The method of molecular dynamics is based on the numerical integration of the Newtonian differential equations for the molecules composing the system. For molecules composed of a single atom, there is no real problem in choosing the dynamical variables as the ordinary cartesian coordinates of the centre of mass provide a suitable set of generalized coordinates. For polyatomic molecules, a number of methods have been employed, including the construction of generalized coordinates, e.g. SHAKE [1, 2] and related methods [3] and the use of Cayley–Klein [4] or quaternion parameters [5, 6]. Most of these methods make use of the variational formulation of Lagrangian dynamics and the use of Lagrange multipliers to perform optimization subject to constraints in the form of either differential or finite equations.

In this article, we present what appears to be two new sets of differential equations for describing the rotational dynamics of rigid bodies which may be solved on a computer without significant error. The generalized coordinates are orthonormal vectors along the principal axes $\vec{u}_1$, $\vec{u}_2$, $\vec{u}_3$ of the rigid body. Since

$$\vec{u}_3 = \vec{u}_1 \times \vec{u}_2 \tag{1.1}$$

these vectors contain only six independent quantities. This is to be compared with four for the quaternion parameters. Since the orientation of a non-axially symmetric molecule can be expressed in terms of three independent quantities (the Euler angles for example), the use of principal axes vectors as dynamical coordinates will also require the use of Lagrange multipliers. It will turn out that the multipliers can be found analytically so that the differential equations can then be integrated with a high order integration algorithm without loss of accuracy (*cf.* SHAKE). Using these vectors as coordinates we obtain the equations of motion in both Lagrangian and Hamiltonian form. For the simple case of a rigid body in two dimensions, we are able to solve these equations analytically in both the Lagrangian and Hamiltonian

formalism and show that the solutions are identical to that given by generalized coordinates.

The method is in fact closely related to an algorithm of Edberg *et al.*[7] and suffers from the same type of instability as that algorithm, namely that small errors in the constraints introduced by roundoffs and errors in the differential equation solver have a tendency to grow as the numerical integration proceeds. However, as we do not consider non-rigid systems, we can utilize the orthonormality of our coordinates to eliminate these errors at each step.

2 DEFINITIONS AND NOTATION

In this section we establish a convenient notation with which we shall describe the motion of a general rigid body under the influence of conservative forces.

2.1 Co-ordinates and the principal axis vectors

We shall define a rigid body as a set of M point masses, $m_1, m_2, \ldots, m_M$ whose positions in (d-dimensional) space are described by vectors $\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_M$. If $\vec{e}_1, \vec{e}_2, \ldots, \vec{e}_M$ form an orthonormal basis for $\mathbb{R}^d$, then we define the d × 1 column vectors $\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_M$ whose elements are the components of the vectors $\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_M$ with respect to the basis thus:

$$[\boldsymbol{r}_i]_j = \vec{r}_i \cdot \vec{e}_j. \tag{2.1}$$

A body is rigid if there are a sufficient number of constraints expressing internal geometrical relations between the positions of the masses. These constraints will typically be of the form

$$\|\vec{r}_i - \vec{r}_j\|^2 = a_{ij}^2 = (\boldsymbol{r}_i - \boldsymbol{r}_j)^T (\boldsymbol{r}_i - \boldsymbol{r}_j) \tag{2.2}$$

expressing the constancy of a bond length a_{ij} or

$$(\boldsymbol{r}_i - \boldsymbol{r}_j)^T (\boldsymbol{r}_k - \boldsymbol{r}_j) = a_{ij} a_{jk} \cos(\theta_{ijk}) \tag{2.3}$$

expressing constancy of the bond angle θ_{ijk} between 2 bonds (ij) and (jk), it being supposed that the lengths of the bonds are also constrained.

It is a straightforward matter to show that constraints of the type (2.3) can be written in the form (2.2) by writing

$$\begin{aligned}(\boldsymbol{r}_i - \boldsymbol{r}_k)^T (\boldsymbol{r}_i - \boldsymbol{r}_k) &= (\boldsymbol{r}_i - \boldsymbol{r}_j - (\boldsymbol{r}_k - \boldsymbol{r}_j))^T (\boldsymbol{r}_i - \boldsymbol{r}_j - (\boldsymbol{r}_j)) \\ &= a_{ij}^2 + a_{jk}^2 - 2a_{ij} a_{jk} \cos(\theta_{ijk}).\end{aligned} \tag{2.4}$$

A sufficient number of constraints to ensure rigidity is given by Md minus the number $\frac{1}{2}d(d-1)$ of independent elements of a $d \times d$ rotation matrix, namely

$$Md - \tfrac{1}{2}d(d-1). \tag{2.5}$$

Let us define the total mass

$$m = \sum_{i=1}^{M} m_i \tag{2.6a}$$

and the position $\vec{R}$ of the centre of mass:

$$\vec{R} = m^{-1} \sum_{i=1}^{M} m_i \vec{r}_i . \tag{2.6b}$$

the moment of inertia about an axis passing through $\vec{R}$ in the direction of the unit vector $\vec{u}$ is

$$I(\vec{u}, \vec{R}) = \sum_{i=1}^{M} m_i [\|\vec{r}_i - \vec{R}\|^2 - \{(\vec{r}_i - \vec{R}) \cdot \vec{u}\}^2] \tag{2.7}$$

or in terms of components

$$I(\boldsymbol{u}, \boldsymbol{R}) = \sum_{i=1}^{M} m_i [(\boldsymbol{r}_i - \boldsymbol{R})^{\mathrm{T}} (\boldsymbol{r}_i - \boldsymbol{R}) - \boldsymbol{u}^{\mathrm{T}} (\boldsymbol{r}_i - \boldsymbol{R}) (\boldsymbol{r}_i - \boldsymbol{R})^{\mathrm{T}} \boldsymbol{u}]. \tag{2.8}$$

the vector $\vec{u}$ is a principal axis vector if it extremizes I subject to the condition $\|\vec{u}\|^2 = 1$, which occurs if

$$\mathbf{A}\mathbf{u} = \lambda \boldsymbol{u}, \tag{2.9}$$

where $\mathbf{A}$ is the real symmetric matrix defined by

$$\boldsymbol{A} = \sum_{i=1}^{M} m_i (\boldsymbol{r}_i - \boldsymbol{R}) (\boldsymbol{r}_i - \boldsymbol{R})^{\mathrm{T}} . \tag{2.10}$$

Thus $\mathbf{u}$ is an eigenvector of $\boldsymbol{A}$ with eigenvalue λ. The vector

$$\vec{u} = \sum_{i=1}^{d} [\boldsymbol{u}]_i \vec{e}_i \tag{2.11}$$

is of course independent of the basis used to compute it. It is relatively straightforward to show that if all the M masses lie on a line, then $\mathbf{A}$ has $(d - 1)$ repeated eigenvalues 0 and if they lie in a plane, there are $(d - 2)$ repeated eigenvalues 0. Because the matrix $\mathbf{A}$ is real and symmetric, the eigenvectors $\vec{u}_1, \vec{u}_2, \ldots, \vec{u}_d$ corresponding to the eigenvalues $\lambda_1, \lambda_2, \ldots, \lambda_d$ form an orthonormal basis for $\mathbb{R}^d$. Now,

$$\sum_{i=1}^{M} m_i (\boldsymbol{r}_i - \boldsymbol{R})^{\mathrm{T}} (\boldsymbol{r}_i - \boldsymbol{R}) = \mathrm{Tr}(\boldsymbol{A}) = \sum_{i=1}^{d} \lambda_i \tag{2.12}$$

so that the moment of inertia corresponding to the eigenvalue λ_i is

$$I(\vec{u}_i, \vec{R}) = \sum_{k \neq i} \lambda_k . \tag{2.13}$$

For each mass m_i, we may write

$$\vec{r}_i = \vec{R} + \sum_{k=1}^{d} x_{ik} \vec{u}_k \tag{2.14}$$

where

$$x_{ik} = (\boldsymbol{r}_i - \boldsymbol{R})^{\mathrm{T}} \boldsymbol{u}_k . \tag{2.15}$$

If we now suppose that the body is translating and rotating, so that the vectors $\vec{r}_i$, $\vec{u}_k$ are functions of time, the quantities x_{ik} are nevertheless numbers independent of time. In what follows, we shall use the $\boldsymbol{u}_i(t)$ as dynamical variables, mindful that they must

satisfy the $\frac{1}{2}d(d+1)$ constraints

$$\boldsymbol{u}_i^{\mathrm{T}}\boldsymbol{u}_j = \delta_{ij}. \tag{2.16}$$

Multiplying Equation (2.15) by m_i and summing over i, we obtain

$$\sum_{i=1}^{M} m_i x_{ik} = 0,\ k = 1, 2, \ldots, d. \tag{2.17}$$

3 CONSTRAINED DYNAMICAL EQUATIONS FOR THE PRINCIPAL AXIS VECTOR

If the rigid body defined in section 2 is in motion, then the vectors $\vec{r}_i$, $\vec{u}_k$ become functions of time t. If $\dot{\vec{r}}_i$, $\dot{\vec{u}}_k$ are the corresponding velocities, then the kinetic energy is

$$T = \frac{1}{2}\sum_{i=1}^{M} m_i \|\dot{\vec{r}}_i\|^2 = \frac{1}{2}\sum_{i=1}^{M} m_i \dot{\boldsymbol{r}}_i^{\mathrm{T}}\dot{\mathbf{r}}_i \tag{3.1}$$

$$= \frac{1}{2}\sum_{i=1}^{M} m_i \|\dot{\vec{R}} + \sum_{k=1}^{d} x_{ik}\dot{\vec{u}}_k\|^2 \tag{3.2}$$

$$= \frac{1}{2} m \|\dot{\vec{R}}\|^2 + \frac{1}{2}\sum_{i=1}^{M} m_i \sum_{k=1}^{d}\sum_{l=1}^{d} x_{ik}x_{il}\dot{\boldsymbol{u}}_k^{\mathrm{T}}\dot{\boldsymbol{u}}_l \tag{3.3}$$

where we have used Equation (2.17). But

$$\sum_{i=1}^{M} m_i x_{ik}x_{il} = \sum_{i=1}^{M} m_i[(\vec{r}_i - \vec{R})\cdot\vec{u}_k][(\vec{r}_i - \vec{R})\cdot\vec{u}_l]$$

$$= \boldsymbol{u}_k^{\mathrm{T}}\boldsymbol{A}\boldsymbol{u}_l \tag{3.4}$$

$$= \lambda_k \delta_{kl}. \tag{3.5}$$

Thus the kinetic energy simplifies to

$$T = \frac{1}{2} m\dot{\boldsymbol{R}}^{\mathrm{T}}\dot{\boldsymbol{R}} + \frac{1}{2}\sum_{k=1}^{d} \lambda_k \dot{\boldsymbol{u}}_k^{\mathrm{T}}\dot{\boldsymbol{u}}_k. \tag{3.6}$$

If the particles composing the rigid body move in some conservative force field with potential $\varphi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_M)$, we have

$$\varphi = \varphi\left(\vec{R} + \sum_{k=1}^{d} x_{1k}\vec{u}_k, \ldots, \vec{R} + \sum_{k=1}^{d} x_{Mk}\vec{u}_k\right). \tag{3.7}$$

Thus we may associate a force $\vec{F}_j$ with each principal axis $\vec{u}_j$, given by

$$\vec{F}_j = -\sum_{i=1}^{M} x_{ij}\nabla_k \varphi \tag{3.8}$$

where $\nabla_k \equiv \partial/\partial\vec{r}_k$ is the usual gradient operator.

3.1 The Euler-Lagrange Equations

A Lagrangian which does not take into account the constraints (2.16) is

$$L(t) = T - \varphi. \tag{3.9}$$

If t_1, t_2 are any two times, then the Euler–Lagrange equations determine trajectories $\vec{R}(t)$, $\vec{u}_1(t)$, . . . , $\vec{u}_d(t)$ for which the integral

$$S = \int_{t_1}^{t_2} L(t')\, dt' \tag{3.10}$$

is an extremum subject to the constraints (2.16). It is shown in standard books o the Calculus of Variations that finite equations of the form (2.16) may be treated using time dependent Lagrange multipliers $\mu_{ij}(t)$ associated with each constraint (2.16), and that the equation of motion for the i'th eigenvector $\vec{u}_i$ with non-zero eigenvalue λ_i is

$$\lambda_i \ddot{\vec{u}}_i = \vec{F}_i - \sum_{k=1}^{d} \mu_{ik}(t)\, \vec{u}_k\,(t). \tag{3.11}$$

Differentiating the constraints (2.16) twice with respect to t, we obtain

$$\vec{u}_i \cdot \ddot{\vec{u}}_j + \ddot{\vec{u}}_i \cdot \vec{u}_j = -2\dot{\vec{u}}_i \cdot \dot{\vec{u}}_j. \tag{3.12}$$

Dividing Equation (3.11) by λ_i and taking the corresponding equation with i replaced with j and using eq. (3.12) gives

$$\mu_{ij}(t) = \frac{(2\lambda_i\lambda_j \dot{\vec{u}}_i \cdot \dot{\vec{u}}_j + \lambda_j \vec{u}_j \cdot \vec{F}_i + \lambda_i \vec{u}_i \cdot \vec{F}_j)}{(\lambda_i + \lambda_j)} \tag{3.13}$$

as an analytic expression for the Lagrange multipliers. These expressions (3.13) may then be inserted into the Euler–Lagrange equations (3.11) to obtain the equations of motion

$$\ddot{\vec{u}}_i = \lambda_i^{-1}\left[\vec{F}_i - \sum_{k=1}^{d} \frac{(2\lambda_i\lambda_k \dot{\vec{u}}_i \cdot \dot{\vec{u}}_k + \lambda_k \vec{u}_k \cdot \vec{F}_i + \lambda_i \vec{u}_i \cdot \vec{F}_k)}{(\lambda_i + \lambda_k)}\right]$$
$$i = 1, \ldots, d\ (\lambda_i \neq 0) \tag{3.14}$$

which form a set of coupled second order differential equations for the vectors $\vec{u}_i(t)$.

3.2 Hamilton's Equations

The equations of motion (3.11) can also be regarded as coming formally from a "Lagrangian"

$$L^*(t) = T - \varphi + \frac{1}{2}\sum_{i=1}^{d}\sum_{j=1}^{d} \gamma_{ij}(t)\,(\vec{u}_i \cdot \dot{\vec{u}}_j + \vec{u}_j \cdot \dot{\vec{u}}_i) \tag{3.15}$$

where

$$\mu_{ij}(t) = \dot{\gamma}_{ij}(t). \tag{3.16}$$

Pursuing this formal equivalence, we define "momenta" $\vec{p}_i$ as

$$\vec{p}_i = \frac{\partial L^*}{\partial \dot{\vec{u}}_i} = \lambda_i \dot{\vec{u}}_i + \sum_{k=1}^{d} \gamma_{ik} \vec{u}_k . \tag{3.17}$$

Using Equations (2.16), we obtain

$$\gamma_{ij} = (\lambda_j \vec{u}_j \cdot \vec{p}_i + \lambda_i \vec{u}_i \cdot \vec{p}_j)/(\lambda_i + \lambda_j) . \tag{3.18}$$

We thus define a "Hamiltonian" function

$$H^* = \sum_{i=1}^{d} \vec{p}_i \cdot \dot{\vec{u}}_i - L^* .$$

It is straightforward (but tedious) to verify that

$$H^* = \frac{1}{2} \sum_{1 \le k < l \le d} \frac{\| \{\vec{p}_k \cdot \vec{u}_l - \vec{p}_l \cdot \vec{u}_k\} \|^2}{(\lambda_k + \lambda_l)} + \varphi . \tag{3.20}$$

Hamilton's equations are then

$$\dot{\vec{p}}_i = -\frac{\partial H^*}{\partial \vec{u}_i} = \sum_{k \neq i} \frac{(\vec{p}_k \cdot \vec{u}_i - \vec{p}_i \cdot \vec{u}_k)\vec{p}_k}{(\lambda_i + \lambda_k)} - \frac{\partial \varphi}{\partial \vec{u}_i} \tag{3.21a}$$

and

$$\dot{\vec{u}}_i = \frac{\partial H^*}{\partial \vec{p}_i} = \sum_{k \neq i} \frac{(\vec{p}_k \cdot \vec{u}_i - \vec{p}_i \cdot \vec{u}_k)\vec{u}_k}{(\lambda_i + \lambda_k)} . \tag{3.21b}$$

The solutions of these equations when substituted back into Equation (3.20) imply that H^* is a constant of the motion.

3.3 An illustrative example

It is by no means clear that these constrained equations of motion (3.14) and (3.21) reduce to traditional equations, but the following simple example shows that they do. Consider a 2-dimensional rigid body with principal axes $\vec{u}_1$, $\vec{u}_2$ and corresponding eigenvalues λ_1, λ_2 rotating in a conservative potential $\varphi(\vec{u}_1, \vec{u}_2)$. If θ represents the angle between $\vec{u}_1$ and the (fixed) unit vector $\vec{e}_1$, then

$$\boldsymbol{u}_1 = \begin{bmatrix} \cos\theta \\ \sin\theta \end{bmatrix}, \quad \boldsymbol{u}_2 = \begin{bmatrix} -\sin\theta \\ \cos\theta \end{bmatrix} \tag{3.22}$$

and using θ as a generalized co-ordinate, we define a Lagrangian

$$L = \frac{1}{2}(\lambda_1 + \lambda_2)\,\dot{\theta}^2 - \varphi(\boldsymbol{u}_1(\theta), \boldsymbol{u}_2(\theta)) \tag{3.23}$$

for which the Euler–Lagrange equation is

$$(\lambda_1 + \lambda_2)\ddot{\theta} = -\frac{\partial \varphi}{\partial \boldsymbol{u}_1} \cdot \frac{d\boldsymbol{u}_1}{d\theta} - \frac{\partial \varphi}{\partial \boldsymbol{u}_2} \cdot \frac{d\boldsymbol{u}_2}{d\theta} \equiv \boldsymbol{F}_1 \cdot \frac{d\boldsymbol{u}_1}{d\theta} + \boldsymbol{F}_2 \cdot \frac{d\boldsymbol{u}_2}{d\theta} . \tag{3.26}$$

Given an explicit form for φ and initial conditions $\theta(0)$, $\dot{\theta}(0)$, this second order ordinary differential equation has a unique solution valid in some region containing $t = 0$.

Consider first the constrained Equation (3.14) with $d = 2$ and suppose that neither

λ_1 nor λ_2 is zero. Then, writing the differential equations out in full,

$$\ddot{\boldsymbol{u}}_1 = \lambda_1^{-1}\left(\boldsymbol{F}_1 - \boldsymbol{u}_1 \frac{(\lambda_1^2 \dot{\boldsymbol{u}}_1^{\mathrm{T}} \mathrm{u}_1 + \lambda_1 \boldsymbol{u}_1^{\mathrm{T}} \boldsymbol{F}_1)}{\lambda_1} - \boldsymbol{u}_2 \frac{(2\lambda_1\lambda_2 \dot{\boldsymbol{u}}_1^{\mathrm{T}} \dot{\boldsymbol{u}}_2 + \lambda_1 \boldsymbol{u}_2^{\mathrm{T}} \boldsymbol{F}_1 + \lambda_1 \boldsymbol{u}_1^{\mathrm{T}} \boldsymbol{F}_2)}{\lambda_1 + \lambda_2}\right) \tag{3.24a}$$

$$\ddot{\boldsymbol{u}}_2 = \lambda_2^{-1}\left(\boldsymbol{F}_2 - \boldsymbol{u}_1 \frac{(2\lambda_1\lambda_2 \dot{\mathrm{u}}_1^{\mathrm{T}} \dot{\boldsymbol{u}}_2 + \lambda_1 \boldsymbol{u}_1^{\mathrm{T}} \boldsymbol{F}_2 + \lambda_2 \boldsymbol{u}_2^{\mathrm{T}} \boldsymbol{F}_1)}{\lambda_1 + \lambda_2} - \boldsymbol{u}_2 \frac{(\lambda_2^2 \dot{\boldsymbol{u}}_2^{\mathrm{T}} \dot{\boldsymbol{u}} + \dot{\boldsymbol{u}}_2 + \lambda_2 \boldsymbol{u}_2^{\mathrm{T}} \boldsymbol{F}_2)}{\lambda_2}\right). \tag{3.24b}$$

It is straightforward but tedious to show that

$$\boldsymbol{u}_1 = \begin{bmatrix} \cos \omega(t) \\ \sin \omega(t) \end{bmatrix}, \quad \boldsymbol{u}_2 = \begin{bmatrix} -\sin \omega(t) \\ \cos \omega(t) \end{bmatrix} \tag{3.25}$$

satisfy these equations if $\omega(t)$ satisfies the differential equation

$$(\lambda_1 + \lambda_2)\,\ddot{\omega} = \boldsymbol{F}_1^{\mathrm{T}} \frac{d\boldsymbol{u}_1}{d\omega} + \boldsymbol{F}_2^{\mathrm{T}} \frac{d\boldsymbol{u}_2}{d\omega} = \boldsymbol{F}_1^{\mathrm{T}} \boldsymbol{u}_2 - \boldsymbol{F}_2^{\mathrm{T}} \boldsymbol{u}_1. \tag{3.26}$$

Thus the result obtained by using generalized coordinates is recovered.

We now show that the Hamilton's Equations (3.21) with $d = 2$ are also satisfied. Writing Equation (3.21b) out in full, we have

$$\dot{\boldsymbol{u}}_1 = \boldsymbol{u}_2 \frac{(\boldsymbol{p}_2^{\mathrm{T}} \boldsymbol{u}_1 - \boldsymbol{p}_1^{\mathrm{T}} \boldsymbol{u}_2)}{(\lambda_1 + \lambda_2)} \tag{3.27a}$$

$$\dot{\boldsymbol{u}}_2 = \boldsymbol{u}_1 \frac{(\boldsymbol{p}_1^{\mathrm{T}} \boldsymbol{u}_2 - \boldsymbol{p}_2^{\mathrm{T}} \boldsymbol{u}_1)}{(\lambda_1 + \lambda_2)} \tag{3.27b}$$

and inserting the forms (3.25), we see that these are identically satisfied if

$$\dot{\omega} = \frac{(\boldsymbol{p}_2^{\mathrm{T}} \boldsymbol{u}_1 - \boldsymbol{p}_1^{\mathrm{T}} \boldsymbol{u}_2)}{(\lambda_1 + \lambda_2)}. \tag{3.28}$$

Differentiating Equation (3.28) with respect to t, and using the expressions (3.21a) for $\dot{\boldsymbol{p}}_1$, $\dot{\boldsymbol{p}}_2$, we find that ω again satisfies the equation (3.26). Thus all three sets of dynamical equations are equivalent.

4 NUMERICAL STABILITY OF THE ALGORITHMS

Although we have demonstrated that the constrained dynamical equations are equivalent to the equations obtained using generalized co-ordinates, numerical errors may build up in any attempt to solve them numerically. Experience shows [7] that this is

the case, so that the constraints become less and less well satisfied as the simulation proceeds. It should be pointed out that at any stage of the process, the errors, introduced are of the order of the machine error ($\sim 10^{-17}$ if double precision arithmetic and a high order integration algorithm are being employed), so that the following crude correction algorithm will ensure that all the constraints are satisfied exactly at each step. Let $\boldsymbol{u}_i^o$, $\dot{\boldsymbol{u}}_i^o$ be the positions and velocities produced after an integration step, and let $\boldsymbol{u}_i$, $\dot{\boldsymbol{u}}_i$ be positions and velocities satisfying all the constraints. Although the $\boldsymbol{u}_i^o$ are only approximately orthonormal, they nevertheless provide a basis for $\mathbb{R}^d$. We thus write

$$u_i = u_i^o + \sum_k \Delta_{ik} \boldsymbol{u}_k^o \tag{4.1}$$

and suppose that the Δ_{ik} are the elements of a symmetric matrix. Then we require

$$\boldsymbol{u}_i^T \boldsymbol{u}_j = \delta_{ij} \simeq \boldsymbol{u}_i^{oT} \boldsymbol{u}_j^o + \Delta_{ij} \boldsymbol{u}_j^{o2} + \Delta_{ji} \boldsymbol{u}_i^{o2}$$

giving

$$\Delta_{ij} = \frac{\delta_{ij} - \boldsymbol{u}_i^{oT} \boldsymbol{u}_j^o}{\boldsymbol{u}_i^{o2} + \boldsymbol{u}_j^{o2}}. \tag{4.2}$$

We stress that this is not the only solution to the problem but merely one which will remove the unwanted numerical errors. The $\boldsymbol{u}_i$ defined by Equation (4.1) will now satisfy the constraints to machine precision and form an orthonormal basis. We write

$$\dot{\boldsymbol{u}}_i = \dot{\boldsymbol{u}}_i^o + \Sigma \varepsilon_{ik} \boldsymbol{u}_k \tag{4.3}$$

where again we suppose that the ε_{ij} form the elements of a symmetric matrix. Then, since we require

$$\boldsymbol{u}_i^T \dot{\boldsymbol{u}}_j + \boldsymbol{u}_j^T \dot{\boldsymbol{u}}_i = 0$$

we obtain

$$\varepsilon_{ij} = -(\boldsymbol{u}_i^T \boldsymbol{u}_j^o + \boldsymbol{u}_j^T \boldsymbol{u}_i^o)/2. \tag{4.4}$$

These simple expedients ensure that all constraints are satisfied indentically.

What we do here should be compared with what is done in methods like SHAKE, where one corrects an initial guess for the new positions which contains non-numerical (i.e. algorithmic) errors. All we are doing here is eliminating small numerical errors caused by finite length floating point arithmetic which will nevertheless grow to unacceptable levels if they remain uncorrected.

5 A NUMERICAL EXAMPLE

We have restricted ourselves to studying the motion of very small systems because we are mainly interested in ensuring that the constraints are maintained in binary collisions. We have studied a relatively long run with 2 and a shorter one with 16 particles, the particles being a 3*CLJ* model for propane. The potential parameters are the same as those normally used for butane and are shown in Table 1. In both cases, truly periodic boundary conditions [8] were employed and the simulations were run on an Olivetti M24 SP personal computer using 64 bit floating point arithmetic.

Table 1 Potential parameters.

Lennard-Jones ε/k_B	62 K
Lennard-Jones σ	0.392 nm
Carbon–Carbon bond length	0.153 nm
Number density ρ	2.5 nm^{-3}

Table 2 2-particle simulation

Number of molecules	2
Time step (Runge–Kutta)	5.2×10^{-16} s
Time step (Predictor–corrector)	2.1×10^{-15} s
Number of time steps	3000
Percentage variation in energy	0.00000003
Maximum deviation of scalar product	10^{-14}

Table 3 16-particle simulation

Number of molecules	16
Time step (Runge–Kutta)	5.2×10^{-16} s
Time step (Predictor–corrector)	2.1×10^{-15} s
Number of time steps	1000
Percentage variation in energy	0.00000001
Maximum deviation of scalar product	10^{-13}

The system was started from a BCC lattice and integrated for 7 time intervals of 5.2×10^{-16} seconds using a fifth order Runge–Kutta algorithm. Thereafter, the integration was continued using a seventh order predictor–corrector algorithm using a time step of 2.1×10^{-15} seconds.

In Tables 2 and 3, we show how the total energy of the system was conserved and indicate how well the constraints were satisfied. As a measure of this latter quantity, we took the maximum absolute deviation of the scalar products of the axes vectors from their exact valeus. We regard the results as satisfactory. It is probably fair to remark that the excellent conservation of energy is due to the fact that forces arising from the truly periodic potential are continuous rather than any virtues of the algorithms employed.

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