

## Modified RATTLE Method for Rigid Body Dynamics in Cartesian Coordinates

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**Abstract.** In this paper, we describe a modified RATTLE (M-RATTLE) method for rigid body dynamics directly in Cartesian coordinates. The M-RATTLE method introduces a new way of resetting the coordinates to satisfy the constraints at each step, which is designed for the rigid body dynamics calculations in the Cartesian coordinates. M-RATTLE is algebraically equivalent to the RATTLE method and the cost of performing rigid body dynamics by M-RATTLE is independent of the number of constraints. The interaction forces between atoms belonging to the same rigid molecule do not need to be computed and explicit expressions of the constraints of internal degrees of freedom are unnecessary. The performance and sampling results of the proposed method are compared with those of the symplectic splitting method for an isolated rigid benz molecule and for a cluster of twenty-seven benz molecules.

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**Key words:** Rigid body dynamics, RATTLE method, symplectic splitting method, Cartesian formulation.

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### 1 Introduction

There has been great interest in developing stable and efficient algorithms for rigid body dynamics, see, e.g., [1–3]. There are three formulations for rigid body dynamics: the rotation matrix formulation, the formulation based on the Euler equations, and the Cartesian formulation [19]. During the past three decades, a number of algorithms have been developed under these formulations, which include the Gear predictor-corrector algorithm [8],

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the linear constraints method [5], the symplectic splitting methods [6,26,29], the symplectic quaternion scheme [22], the leapfrog scheme [25], the symplectic constrained rotation matrix integration [15,21] and the algorithm proposed by Neto et al. [24].

For rigid molecules whose potentials are expressed in terms of interactions between atomic sites, it is natural to consider calculating the rigid body dynamics directly in Cartesian coordinates. The Cartesian formulation is believed to have good stability property, which can also avoid many complications of Euler equations and quaternions. In the Cartesian formulation, the dynamics are determined by integrating the equations of motion of each atom, subject to the constraints that make the molecules rigid (constraining all internal degrees of freedom). The equations of motion of constrained dynamics are

$$\begin{cases} M\ddot{X}(t) = -\frac{\partial U(X(t))}{\partial X} - \frac{\partial g(X(t))}{\partial X}^T \lambda, \\ g(X(t)) = 0, \end{cases} \quad (1.1)$$

where  $M = \text{diag}\{m_1, m_1, m_1, \dots, m_N, m_N, m_N\}$  is the  $3N \times 3N$  mass matrix,  $N$  is the number of atoms,  $m_i$  is the mass of atom  $i$ ,  $X$  is the coordinate of all atoms,  $U(X)$  is the potential,  $g$  is the  $m$ -dimensional vector of constraints,  $\lambda$  is the  $m$  vector of Lagrange multipliers, and  $m$  is the number of constraints. The underlying system of ordinary differential equations,

$$\ddot{X} = (I - M^{-1}B^T(BM^{-1}B^T)^{-1}B)M^{-1}F - M^{-1}B^T(BM^{-1}B^T)^{-1}\frac{dB}{dt}\dot{X}, \quad (1.2)$$

is equivalent to (1.1) provided that the matrix  $BM^{-1}B^T$  is invertible, where  $B = \partial g(X)/\partial X$  and  $F = -\partial U(X)/\partial X$ . If the initial values  $X(0)$  and  $\dot{X}(0)$  satisfy the constraints, then solutions of (1.2) will continue to satisfy the constraints. In practice, we can discretize (1.2) directly, but the numerical error leads to drifts of the constraints. This is why we prefer SHAKE or RATTLE which are direct discretizations of the equations (1.1).

In [27], Rychaert et al. proposed SHAKE discretization for (1.1) based on the leap-frog Verlet scheme,

$$\begin{cases} MV_{n+1/2} = MV_{n-1/2} + hF_n - hB_n^T \lambda_n, \\ X_{n+1} = X_n + hV_{n+1/2}, \\ g(X_{n+1}) = 0, \end{cases} \quad (1.3)$$

where  $F_n = -\partial U(X_n)/\partial X$  and  $B_n = \partial g(X_n)/\partial X$ ,  $h$  is the size of the time-step, and  $\{X_n, V_n\}$  are the coordinates and velocities of all atoms at step  $n$ . An alternative velocity-level formulation, RATTLE, was proposed by Andersen [1]:

$$\begin{cases} MV_{n+1/2} = MV_n + hF_n/2 - hB_n^T \lambda_n/2, \\ X_{n+1} = X_n + hV_{n+1/2}, \\ g(X_{n+1}) = 0, \\ MV_{n+1} = MV_{n+1/2} + hF_{n+1}/2 - hB_{n+1}^T \lambda_{n+1}^v/2, \\ B_{n+1}V_{n+1} = 0. \end{cases} \quad (1.4)$$

In RATTLE, the hidden constraints

$$\frac{dg(X(t))}{dt} = \frac{\partial g}{\partial X} \dot{X} = 0$$

are satisfied at each step. RATTLE is symplectic and SHAKE, while not symplectic, yields solutions with atomic positions identical to those of RATTLE and slightly perturbed velocities [18]. In SHAKE and RATTLE, the equations of constraints  $g(X_{n+1}) = 0$  need to be solved to get the Lagrange multipliers  $\lambda_n$ . This is usually done by SHAKE iteration or quasi-Newton iteration [2]. There are also other methods developed for the constrained dynamics, such as the EEM method [7], the LINCS method [11], the NIMM method [28,30,31], the M-SHAKE method [16], the WIGGLE method [17] and the SETTLE method [23]. These methods are addressed to constrained dynamics but obviously cover the case when all the internal degrees of freedom are constrained. The existing methods for the constrained dynamics under the Cartesian formulation are not suitable for computing the rigid body dynamics for general molecules, since the number of constraints increases dramatically. This makes the cost of computation too high for large molecules and some of them have convergence problems when constraints of bond-angles are involved [10–12].

Besides the methods for the constrained dynamics, the linear constraints method in [5] is a method for the rigid body dynamics under the Cartesian formulation. It chooses the basic atoms such that the three additional linear constraint relations for each atom are not included in the basic set. Moreover, it needs to invert a  $(3N-4)$ -dimensional matrix at the beginning of the simulation.

In [6], a symplectic splitting method is presented by integrating the orientation of the rigid body through a sequence of planar rotations. It is shown in [6,19,24] that the symplectic splitting method in [6] is better than those based on quaternions and constraining rotation matrix, and the conservation of the total energy is practically identical to those obtained by the procedures of [5,24]. It is pointed out that a recent review article on symplectic algorithms can be found in [20]. Moreover, [24] shows that the accuracy provided by the leapfrog scheme in [25] is lower than that provided by the methods given in [5,24].

The M-RATTLE method [4] is ideally suited for performing the rigid body dynamics for general molecules under the Cartesian coordinates directly. The method is algebraically equivalent to the RATTLE method, so energy conservation can be achieved. Its cost is independent of the number of constraints. Moreover, it requires to solve a 3-dimensional eigenvector problem and a 6-dimensional linear system at each iteration for correcting the coordinates to satisfy the constraints of all internal degrees of freedom. The interaction forces between atoms belonging to the same rigid molecule does not need to be computed and the explicit expressions of the  $3N-6$  constraints are unnecessary.

This paper is organized as follows. In Section 2, we present the M-RATTLE method for rigid body dynamics. Two numerical examples, one for one isolated rigid benz molecule in vacuum and the other for a cluster of twenty-seven rigid benz molecules, are presented in Section 3. The final section will give some concluding remarks.

## 2 The M-RATTLE method

For simplicity, we consider rigid body dynamics for one  $N$ -atom macromolecule. It is straightforward to generalize the algorithm to the case of rigid body dynamics with more than one macromolecule. Constraining one  $N$ -atom macromolecule as a rigid body is equivalent to constraining  $3N-6$  independent distances between the atom pairs corresponding to the  $3N-6$  internal degrees of freedom. Assume the  $i$ th equation of the constraint is

$$\|\vec{X}_{i_1} - \vec{X}_{i_2}\|_2^2 - l_{i_1 i_2}^2 = 0, \quad (2.1)$$

where  $\vec{X}_{i_1}$  and  $\vec{X}_{i_2}$  are the position vectors of the atoms  $i_1$  and  $i_2$  involved in the constraint  $i$ , and  $l_{i_1 i_2}$  is the equivalent value of the distance between the atom  $i_1$  and  $i_2$ . Let

$$\begin{aligned} g_i &= \|\vec{X}_{i_1} - \vec{X}_{i_2}\|_2^2 - l_{i_1 i_2}^2, \quad i = 1, \dots, 3N-6, \\ g &= (g_1, \dots, g_{3N-6})^T, \quad B(X) = \frac{\partial g(X)}{\partial X}. \end{aligned} \quad (2.2)$$

Suppose we have the positions and velocities  $\{X_n, V_n\}$  at step  $n$ , with  $g(X_n) = 0$  together with hidden constraints  $B(X_n)V_n = 0$ . We obtain the positions and velocities  $\{X_{n+1}, V_{n+1}\}$  at the next time-step through the following three-step procedure: unconstrained step, correction, and velocity propagation.

### 2.1 Unconstrained step

In M-RATTLE, the unconstrained step is given by

$$X_{n+1}^p = X_n + V_n h + M^{-1/2}(I - \mathcal{P}_n)M^{-1/2}F_n h^2/2, \quad (2.3)$$

where  $h$  is the time-step,  $F_n$  is the force at step  $n$ , and

$$\mathcal{P}_n = \mathcal{P}(X_n) = M^{-1/2}B_n^T(B_n M^{-1}B_n^T)^{-1}B_n M^{-1/2}. \quad (2.4)$$

Here  $\mathcal{P}_n$  is the projection operator from  $\mathbb{R}^{3N}$  to the  $(3N-6)$ -dimensional subspace

$$\text{span}\{M^{-1/2}b_1^{nT}, \dots, M^{-1/2}b_{3N-6}^{nT}\},$$

where  $b_i^n$  is the  $i$ th row of  $B_n$ ,  $B_n = B(X_n)$ . The equations (2.3) can be viewed as a discretization of the underlying ordinary differential equations (1.2) with the last term  $-M^{-1}B^T(BM^{-1}B^T)^{-1}\frac{dB}{dt}\dot{X}$  in (1.2) omitted.

Define  $U^{ex}(X)$  by

$$U^{ex}(X) = U(X) - U^{in}(X), \quad (2.5)$$

where  $U^{in}(X)$  is the potential which depends only on the internal degrees of freedom of the whole molecule and is a function of  $g$ , i.e.  $U^{in} = U^{in}(g)$ . Define  $F^{ex}(X)$  by

$$F^{ex}(X) = -\frac{\partial U^{ex}(X)}{\partial X}, \quad (2.6)$$

which is the vector of external forces acting on the atoms. Define  $F^{in}$  by

$$F^{in}(X) = -\frac{\partial U^{in}(X)}{\partial X}, \quad (2.7)$$

which is the vector of internal forces acting on the atoms, i.e. the interaction forces between atoms belonging to the same rigid molecule. From (2.5)-(2.7), we have

$$F(X) = -\frac{\partial U(X)}{\partial X} = F^{in}(X) + F^{ex}(X). \quad (2.8)$$

Let  $\tilde{F}_n = M^{-1/2}(I - \mathcal{P}_n)M^{-1/2}F_n$ . Actually,  $\tilde{F}_n = M^{-1/2}(I - \mathcal{P}_n)M^{-1/2}F_n^{ex}$ . This can be explained as follows:

$$\begin{aligned} M^{-1/2}(I - \mathcal{P}_n)M^{-1/2}F_n^{in} &= M^{-1/2}(I - \mathcal{P}_n)M^{-1/2}\left(-\frac{\partial U^{in}(g(X_n))}{\partial X}\right) \\ &= M^{-1/2}(I - \mathcal{P}_n)M^{-1/2}\left(-B_n^T \frac{\partial U^{in}(g)}{\partial g}\right) = 0. \end{aligned} \quad (2.9)$$

Hence,

$$\begin{aligned} \tilde{F}_n &= M^{-1/2}(I - \mathcal{P}_n)M^{-1/2}F_n \\ &= M^{-1/2}(I - \mathcal{P}_n)M^{-1/2}(F_n^{in} + F_n^{ex}) \\ &= M^{-1/2}(I - \mathcal{P}_n)M^{-1/2}F_n^{ex}. \end{aligned} \quad (2.10)$$

That is to say, we do not need to compute the interaction forces between the atoms belonging to the same rigid molecule for the rigid body dynamics.

## 2.2 The correction step

The objective of the correction step is to make the coordinates at step  $n+1$  fulfill the constraints with a user-specified error tolerance  $\epsilon$ , i.e.  $\|g(X_{n+1})\| < \epsilon$ . The correction  $X_{n+1} - X_{n+1}^p$  should satisfy the following condition:

$$X_{n+1} - X_{n+1}^p \in \text{span}\{M^{-1}b_1^{nT}, \dots, M^{-1}b_{3N-6}^{nT}\}, \quad (2.11)$$

where  $b_i^n$  is the  $i$ th row of  $B_n = \frac{\partial g(X)}{\partial X}|_{X=X_n}$ . As shown in the original paper on M-RATTLE [4], this condition makes the correction to be equivalent to calculating the Lagrange multipliers in the RATTLE discretization (1.4). In practice, the correction is done as follows:

(1) Initialize  $X_{n+1}^1 = X_{n+1}^p$  and let  $k=1$ .

- (2) Align  $X_n$  to  $X_{n+1}^k$  by Kabsch's algorithm [13, 14], i.e. find a  $3 \times 3$  orthogonal matrix  $u_k^{n+1}$  which minimizes the function

$$\|U_k^{n+1}(X_n - X_n^c) - (X_{n+1}^k - X_{n+1}^{kc})\|_2^2, \quad (2.12)$$

where  $U_k^{n+1}$  is a  $3N \times 3N$  block diagonal matrix,  $U_k^{n+1} = \text{diag}\{u_k^{n+1}, \dots, u_k^{n+1}\}$ ,  $X_n^c$  and  $X_{n+1}^{kc}$  are two  $3N$ -vectors of the form  $X_n^c = (\vec{X}_n^{cT}, \dots, \vec{X}_n^{cT})^T$  and  $X_{n+1}^{kc} = (\vec{X}_{n+1}^{kcT}, \dots, \vec{X}_{n+1}^{kcT})^T$ ,  $\vec{X}_n^c$  and  $\vec{X}_{n+1}^{kc}$  are the position vectors for the mass center of the configurations  $\{X_n\}$  and  $\{X_{n+1}^k\}$ , respectively. Let  $\hat{X}_{n+1}^k = U_k^{n+1}(X_n - X_n^c) + X_{n+1}^{kc}$ .

The Kabsch's algorithm is described briefly as follows:

- (a) Let  $Z_n = X_n - X_n^c$  and  $Z_{n+1}^k = X_{n+1}^k - X_{n+1}^{kc}$ . Suppose

$$Z_n = (z_{x_1}^n, z_{y_1}^n, z_{z_1}^n, \dots, z_{x_N}^n, z_{y_N}^n, z_{z_N}^n), \quad (2.13)$$

$$Z_{n+1}^k = (z_{x_1}^{n+1,k}, z_{y_1}^{n+1,k}, z_{z_1}^{n+1,k}, \dots, z_{x_N}^{n+1,k}, z_{y_N}^{n+1,k}, z_{z_N}^{n+1,k}), \quad (2.14)$$

where  $N$  is the number of atoms. Let

$$D_{n+1}^k = \begin{pmatrix} D_{xx}^{n+1,k} & D_{xy}^{n+1,k} & D_{xz}^{n+1,k} \\ D_{yx}^{n+1,k} & D_{yy}^{n+1,k} & D_{yz}^{n+1,k} \\ D_{zx}^{n+1,k} & D_{zy}^{n+1,k} & D_{zz}^{n+1,k} \end{pmatrix}, \quad (2.15)$$

where  $D_{\alpha\beta}^{n+1,k} = \sum_{i=1}^N z_{\alpha i}^{n+1,k} z_{\beta i}^{n+1,k}$ ,  $\alpha, \beta \in \{x, y, z\}$ .

- (b) Determine the three eigenvalues  $u_1^{n+1,k} \geq u_2^{n+1,k} \geq u_3^{n+1,k}$  and the corresponding orthogonal eigenvectors  $a_1^{n+1,k}$ ,  $a_2^{n+1,k}$  and  $a_3^{n+1,k}$  of the matrix  $D_{n+1}^{kT} D_{n+1}^k$ . Let  $\tilde{a}_3^{n+1,k} = a_1^{n+1,k} \times a_2^{n+1,k}$  and  $\tilde{A}^{n+1,k} = (a_1^{n+1,k}, a_2^{n+1,k}, \tilde{a}_3^{n+1,k})^T$ .

- (c) Let

$$c_1^{n+1,k} = D_{n+1}^k a_1^{n+1,k} / \|D_{n+1}^k a_1^{n+1,k}\|_2, \quad c_2^{n+1,k} = D_{n+1}^k a_2^{n+1,k} / \|D_{n+1}^k a_2^{n+1,k}\|_2, \\ c_3^{n+1,k} = (c_1^{n+1,k} \times c_2^{n+1,k}) / \|c_1^{n+1,k} \times c_2^{n+1,k}\|_2, \quad C^{n+1,k} = (c_1^{n+1,k}, c_2^{n+1,k}, c_3^{n+1,k}).$$

- (d) Let

$$u_k^{n+1} = C^{n+1,k} \tilde{A}^{n+1,k}. \quad (2.16)$$

- (3) Let

$$X_{n+1}^{k+1} = X_{n+1}^k + M^{-1/2} \mathcal{P}_n M^{1/2} (\hat{X}_{n+1}^k - X_{n+1}^k). \quad (2.17)$$

If  $\|\hat{X}_{n+1}^k - X_{n+1}^k\| > \epsilon$ , then let  $k = k + 1$ , and goto Step (2). If  $\|\hat{X}_{n+1}^k - X_{n+1}^k\| < \epsilon$ , then let  $X_{n+1} = X_{n+1}^{k+1}$ .

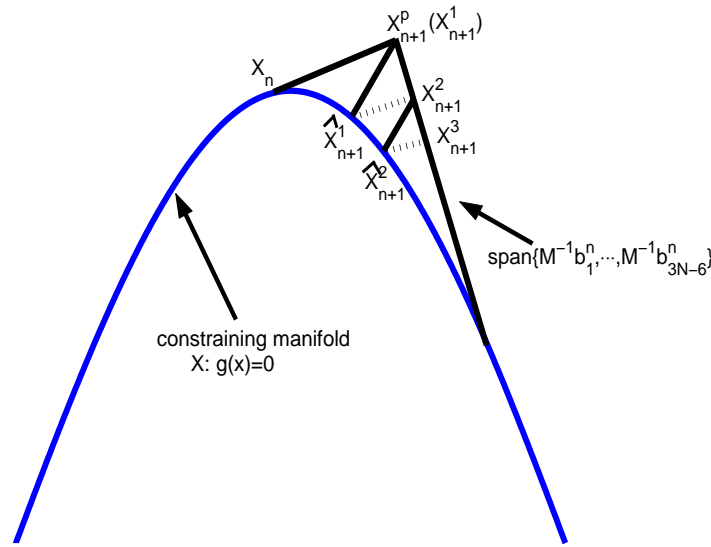


Figure 1: A schematic picture of the first two iterations of the correction step.

In Step (2), since  $\hat{X}_{n+1}^k$  is obtained by aligning  $X_n$  to  $X_{n+1}^k$  and  $X_n$  satisfies the constraints,  $\{\hat{X}_{n+1}^k\}$  is the configuration which has the least distance to  $\{X_{n+1}^k\}$  on the constraining manifold:  $\{X: g(X) = 0\}$ . If we let  $X_{n+1}^{k+1} = X_{n+1}^k + (\hat{X}_{n+1}^k - X_{n+1}^k)$ , it can be viewed as correcting the  $X_{n+1}^k$  to satisfy the constraints exactly. However, it does not satisfy the condition (2.11). So we project the correction  $(\hat{X}_{n+1}^k - X_{n+1}^k)$  to the subspace  $\text{span}\{M^{-1}b_1^{nT}, M^{-1}b_2^{nT}, \dots, M^{-1}b_{3N-6}^{nT}\}$  by  $M^{-1/2}\mathcal{P}_n M^{1/2}(\hat{X}_{n+1}^k - X_{n+1}^k)$ , and this should be done iteratively to achieve good accuracy for the equations of constraints. Fig. 1 shows a schematic picture of the first two iterations of the correction procedure.

The cost of the correction comes mainly from solving a  $3 \times 3$  eigenvector problem in Kabsch's algorithm and computing the projection

$$M^{-1/2}\mathcal{P}_n M^{1/2}(\hat{X}_{n+1}^k - X_{n+1}^k)$$

at each iteration of the correction.

### 2.3 Propagating the velocities

Note that the hidden constraint  $B_{n+1}V_{n+1}=0$  is linear with respect to  $V_{n+1}$ . Consequently, the value of  $\lambda_{n+1}^v$  in the RATTLE method (1.4) can be computed explicitly provided that  $X_{n+1}$  is known. For the same reasons mentioned in Section 2.1, we do not need to compute the internal forces at step  $n+1$ . Therefore, the last two steps of RATTLE (1.4) can be rewritten as

$$V_{n+1} = (I - M^{-1/2}\mathcal{P}_{n+1}M^{1/2})((X_{n+1} - X_n)/h + hM^{-1}F_{n+1}^{ex}/2), \quad (2.18)$$

where

$$\mathcal{P}_{n+1} = \mathcal{P}(X_{n+1}) = M^{-1/2} B_{n+1}^T (B_{n+1} M^{-1} B_{n+1}^T)^{-1} B_{n+1} M^{-1/2}, \quad (2.19)$$

$B_{n+1} = \frac{\partial g(X)}{\partial X} |_{X=X_{n+1}}$ ,  $F_{n+1}^{ex}$  is the vector of the external forces acting on the atoms at step  $n+1$ ,  $h$  is the time-step, and  $M$  is the mass matrix.

## 2.4 The projection operator $\mathcal{P}_n$

The projection operator  $\mathcal{P}_n$  is often used. It is a projection operator from  $\mathbb{R}^{3N}$  to the  $(3N-6)$ -dimensional subspace

$$\text{span}\{M^{-1/2} b_1^{nT}, \dots, M^{-1/2} b_{3N-6}^{nT}\},$$

where  $b_i^n$  is the  $i$ th row of  $B_n = \frac{\partial g(X_n)}{\partial X}$ . If  $\mathcal{P}_n$  is computed by

$$\mathcal{P}_n = M^{-1/2} B_n^T (B_n M^{-1} B_n^T)^{-1} B_n M^{-1/2}, \quad (2.20)$$

then we need to solve a  $(3N-6) \times (3N-6)$  linear system whose coefficient matrix is given by  $B_n M^{-1} B_n^T$ . Assume we have the 6 bases  $w_1^n, \dots, w_6^n$  of the 6-dimensional orthogonal complementary subspace  $\text{span}\{M^{-1/2} b_1^{nT}, \dots, M^{-1/2} b_{3N-6}^{nT}\}^\perp$ , i.e.  $W_n M^{-1/2} B_n^T = 0$ , where  $W_n$  is a  $6 \times 3N$  matrix whose rows are  $w_1^n, \dots, w_6^n$ . Then  $\mathcal{P}_n$  can be computed by

$$\mathcal{P}_n = I - W_n^T (W_n W_n^T)^{-1} W_n. \quad (2.21)$$

Computing  $\mathcal{P}_n$  by (2.21) only requires to solve a linear system related to the  $6 \times 6$  coefficient matrix  $W_n W_n^T$ . Actually, the bases  $w_1^n, \dots, w_6^n$  can be expressed explicitly. Define

$$T_i = \begin{pmatrix} m_i^{\frac{1}{2}} & 0 & 0 \\ 0 & m_i^{\frac{1}{2}} & 0 \\ 0 & 0 & m_i^{\frac{1}{2}} \end{pmatrix}, \quad (2.22)$$

$$R_i^n = \begin{pmatrix} 0 & -m_i^{\frac{1}{2}} z_i^n & m_i^{\frac{1}{2}} y_i^n \\ m_i^{\frac{1}{2}} z_i^n & 0 & -m_i^{\frac{1}{2}} x_i^n \\ -m_i^{\frac{1}{2}} y_i^n & m_i^{\frac{1}{2}} x_i^n & 0 \end{pmatrix}, \quad (2.23)$$

$$A_i^n = \begin{pmatrix} T_i \\ R_i^n \end{pmatrix}, \quad (2.24)$$

where  $m_i$  is the mass of the  $i$ th atom and  $(x_i^n, y_i^n, z_i^n)$  is the coordinate for the  $i$ th atom of the configuration  $\{X_n\}$ . Let

$$W_n = (A_1^n, \dots, A_N^n). \quad (2.25)$$

The rows of  $W_n$  are the translational and rotational modes of the configuration  $\{X_n\}$  [32] and it is easy to verify that

$$W_n M^{-1/2} b_{i,j}^{nT} = 0, \quad i \neq j \text{ and } i, j \in \{1, \dots, N\}, \quad (2.26)$$



where

$$b_{i,j}^n = \frac{\partial \|\vec{X}_i^n - \vec{X}_j^n\|_2^2}{\partial X_n}, \quad \vec{X}_i^n = (x_i^n, y_i^n, z_i^n)^T$$

is the position vector of the  $i$ th atom of the configuration  $\{X_n\}$ . So  $W_n M^{-1/2} B_n^T = 0$  and  $W_n$  is the matrix we need. For the linear molecule, the rank of  $(A_1^n, \dots, A_N^n)$  is equal to 5. Then we let  $W_n$  be the  $5 \times 3N$  matrix whose rows are the first 5 rows of  $(A_1^n, \dots, A_N^n)$ .

## 2.5 The M-RATTLE method for rigid body dynamics

With above preparations, the M-RATTLE method for rigid body dynamics in the Cartesian coordinates is as follows.

**(1)** At the first step, give the initial coordinates and velocities  $\{X_0, V_0\}$ . Set

$$V_0 = M^{-1/2} W_0^T (W_0 W_0^T)^{-1} W_0 M^{1/2} V_0, \quad (2.27)$$

to make the initial velocities  $V_0$  satisfy the hidden constraints  $B_0 V_0 = 0$ . Here  $W_0$  is defined as in (2.22)-(2.25) by substituting  $X_0$  for  $X_n$ , and  $M$  is the mass matrix.

**(2)** At step  $n$  ( $n \geq 0$ ), suppose we have the coordinates and velocities  $\{X_n, V_n\}$ .

**(a)** Let

$$X_{n+1}^p = X_n + V_n h + M^{-1/2} W_n^T (W_n W_n^T)^{-1} W_n M^{-1/2} F_n^{ex} h^2 / 2, \quad (2.28)$$

where  $W_n$  is defined as in (2.22)-(2.25),  $F_n^{ex}$  is the vector of the external forces acting on atoms at step  $n$ ,  $h$  is the time-step, and  $M$  is the mass matrix.

**(b)** Initialize  $X_{n+1}^1 = X_{n+1}^p$ , and let  $k = 1$ .

**(b1)** Get  $\hat{X}_{n+1}^k$  through aligning  $X_n$  to  $X_{n+1}^k$  by Kabsch's algorithm.

**(b2)** Let

$$X_{n+1}^{k+1} = X_{n+1}^k + (I - M^{-1/2} W_n^T (W_n W_n^T)^{-1} W_n M^{1/2}) (\hat{X}_{n+1}^k - X_{n+1}^k). \quad (2.29)$$

If  $\|\hat{X}_{n+1}^k - X_{n+1}^k\| \geq \epsilon$ , goto Step **(b1)** and set  $k = k + 1$ . If  $\|\hat{X}_{n+1}^k - X_{n+1}^k\| < \epsilon$ , then let  $X_{n+1} = X_{n+1}^{k+1}$ .

**(c)** Let

$$V_{n+1} = M^{-1/2} W_{n+1}^T (W_{n+1} W_{n+1}^T)^{-1} W_{n+1} M^{1/2} ((X_{n+1} - X_n) / h + h M^{-1} F_{n+1}^{ex} / 2), \quad (2.30)$$

where  $W_{n+1}$  is defined as in (2.22)-(2.25) by substituting  $X_{n+1}$  for  $X_n$ , and  $F_{n+1}^{ex}$  is the vector of the external forces acting on atoms at step  $n + 1$ .

From the above description, we observe that M-RATTLE dose not need the explicit expressions of the internal constraints.

### 3 Numerical examples

#### 3.1 One benz molecule

In this subsection we choose one isolated rigid benz molecule in vacuum as a first benchmark for our integration scheme. A benz molecule has a six-atom ring, which is very rigid due to its special chemical structure. So constraining it as a rigid body is commonly done in practice. We performed dynamical simulations for one rigid benz with different time-steps to compare the effectiveness of M-RATTLE with the symplectic splitting method of [6].

The initial velocities are first sampled from a normalized Gaussian distribution, then the linear momentum is set to zero and the velocities are set to satisfy the hidden constraints by (2.27). Moreover, the initial kinetic energy is scaled to be  $12.08 \text{ kcal/mol}$ . The stopping criteria for the correction step is

$$\|\hat{X}_{n+1}^k - X_{n+1}^k\|_1 < 10^{-12}. \quad (3.1)$$

The simulations are all done with 100,000 steps. The LU-factorization method [9] is used for solving the relevant linear equations in M-RATTLE. The simulations are performed on a PC with 256 MB of memory and 1.2GHz processing speed. The energy fluctuation defined by  $E_{flu} = \sqrt{\langle E^2 \rangle - \langle E \rangle^2} / |\langle E \rangle|$  is taken as the main criterion for the validity of the simulations.

Fig. 2 shows that the energy fluctuations of symplectic splitting method and M-RATTLE are quite different for an isolated benz in vacuum. For the symplectic splitting method, the fluctuations are about  $10^{-6}$ ,  $10^{-5}$  and  $10^{-4}$ , using time-steps of  $5fs$ ,  $10fs$  and  $15fs$  respectively. For M-RATTLE, the fluctuations range from  $10^{-14}$  to  $10^{-12}$ . This is explained as follows. For an isolated rigid benz in vacuum, there is no external force and the potential remains constant since the molecule is constrained rigid. In such a situation, both RATTLE and M-RATTLE conserve the kinetic energy strictly if the equations of constraints are solved exactly at each step, while the symplectic splitting method does not. Therefore, the energy fluctuations of M-RATTLE remain very small since the equations of constraints are satisfied to finite precision at each step.

For these simulations, the CPU times cost by the symplectic splitting method remain 11.2 seconds and those by M-RATTLE are 13.8 seconds, 15.1 seconds and 17.3 seconds, using time-steps of  $5fs$ ,  $10fs$  and  $15fs$ , respectively. This is because the symplectic splitting method is explicit and M-RATTLE needs to solve the equations of constraints iteratively at each step. Moreover, for the one benz molecule problem, there is no external force and the main cost of M-RATTLE comes from solving the equations of constraints at each step. When the time-step is large, M-RATTLE needs more iteration loops to solve the equations of constraints. In these simulations, the average numbers of iterations at each step of M-RATTLE are 4, 5 and 6 using time-steps of  $5fs$ ,  $10fs$  and  $15fs$ , respectively.

The sampling of the rigid body dynamics of the isolated benz molecule using the

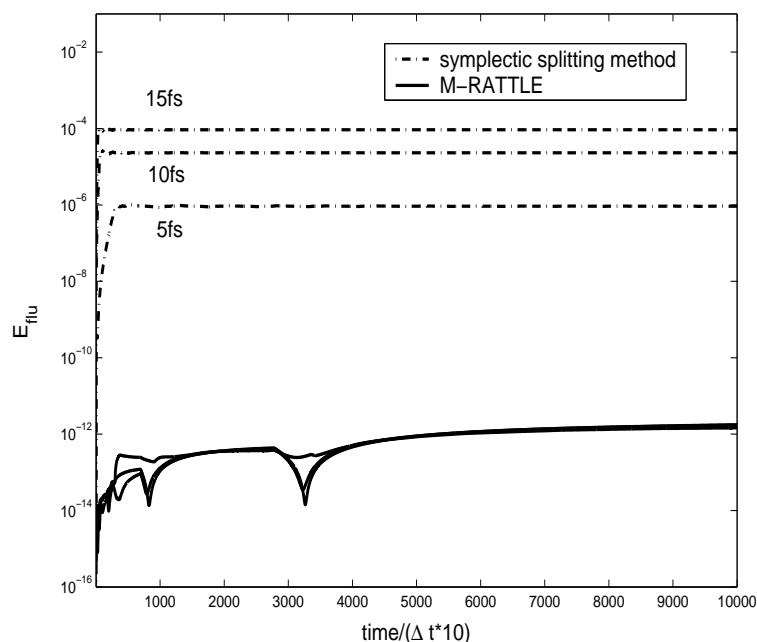


Figure 2: Energy fluctuations of 100000 steps of dynamical simulations for an isolated rigid benz molecules in vacuum, with time-steps ranging from 5fs to 15fs. Calculations carried out with the M-RATTLE method (solid lines) and with the symplectic splitting method (dotted lines) of [6].

M-RATTLE method and the symplectic splitting method of [6] are also studied. Define

$$q^n = \frac{\vec{X}_H^n - \vec{X}_n^c}{\|\vec{X}_H^n - \vec{X}_n^c\|_2}, \quad (3.2)$$

where  $\vec{X}_H^n$  is the position vector of one selected hydrogen atom of the benz molecule at step  $n$ , and  $\vec{X}_n^c$  is the position vector of the mass center of the benz molecule at step  $n$ . The normalized vector  $q^n$  represents the orientation of the benz molecule at step  $n$ . Figs. 3 and 4 show the distributions of components of  $q^n$  using M-RATTLE and the symplectic splitting, respectively. The simulations are all done for 500ps, with the time-step is 5fs. From these figures we can see that the distributions produced by M-RATTLE are more reasonable than those produced by the symplectic splitting method.

### 3.2 A cluster of twenty-seven rigid benz molecules

To compare our method with the symplectic splitting method in [6] for more general cases, we performed simulations for a cluster of twenty-seven rigid benz molecules with different time-steps. The initial temperature is set to 300K, and the other initial settings are the same as in the former example. The CHARMM force field is used [3].

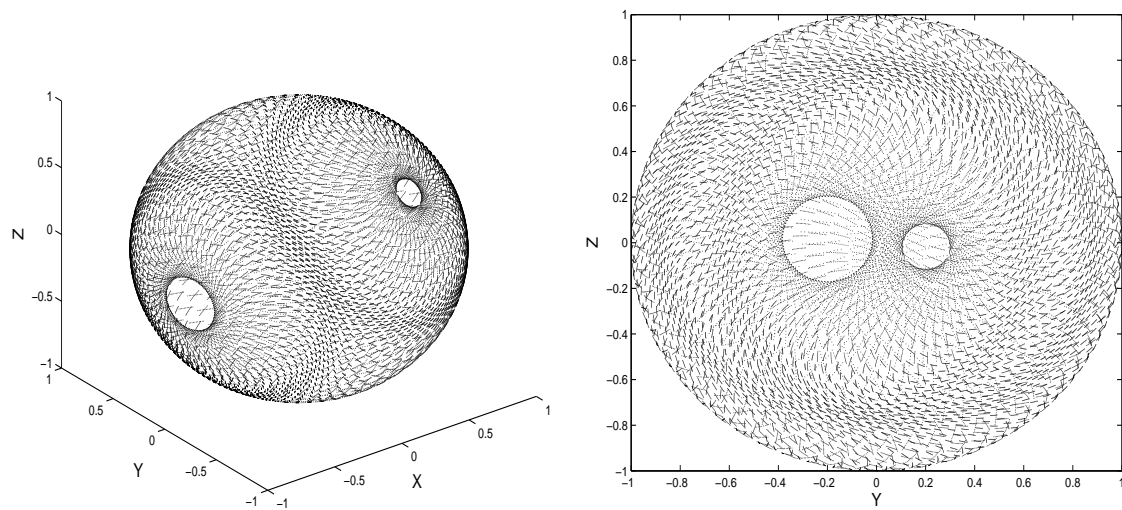


Figure 3: Distributions of the components of  $q^n$ , using the M-RATTLE method.

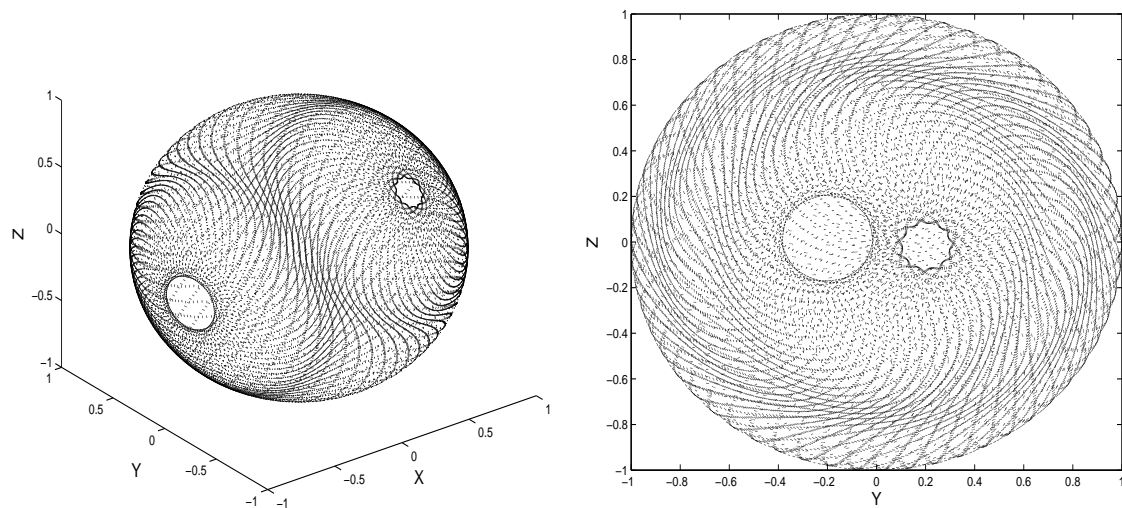


Figure 4: Distributions of the components of  $q^n$ , using the symplectic splitting method.

Fig. 5 shows that the M-RATTLE method and the symplectic splitting method of [6] both lead to stable energy conservations and the magnitudes of the fluctuation for both methods are of the same order. In these simulations, the CPU times cost by the symplectic splitting method remain 4775.4 seconds for different time-steps and those by M-RATTLE are 5283.1 seconds, 5287.7 seconds and 5290.2 seconds, using time-steps of  $5fs$ ,  $10fs$  and  $15fs$ , respectively. The average iteration numbers at each step with the three time-steps for each benz are 3.35, 4.42, 4.51, respectively.

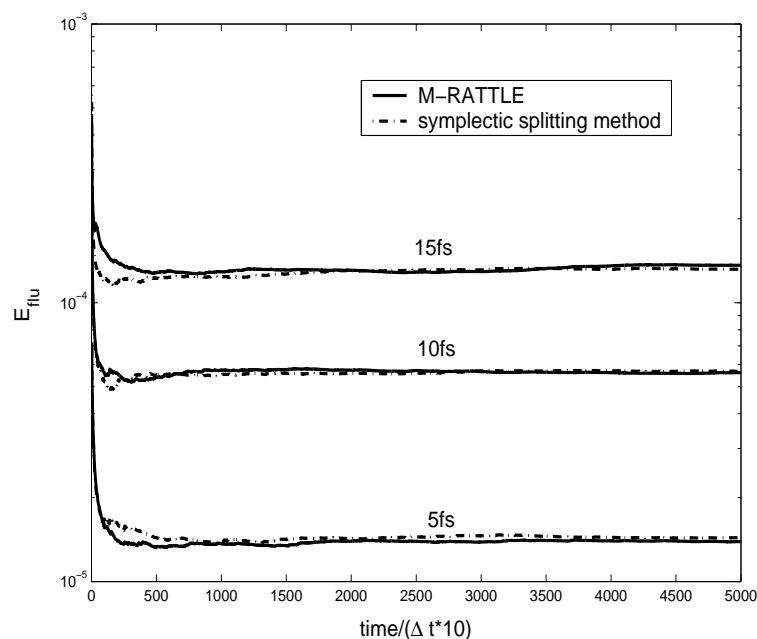


Figure 5: Energy fluctuations of 50000 steps of dynamical simulations for a cluster of twenty-seven benz molecules, with time-steps ranging from 5fs to 15fs. Calculations carried out with the M-RATTLE method (solid lines) and with the symplectic splitting method (dotted lines) of [6].

## 4 Conclusion

The proposed M-RATTLE is a modified version of the RATTLE method, which is ideally suited for performing rigid body dynamics for general macromolecules in Cartesian coordinates. It is not necessary for M-RATTLE to compute the internal forces, so the explicit expressions of internal constraints are not required. The proposed method only needs to solve a  $3 \times 3$  eigenvector problem and a 6-dimensional linear system at each iteration step for resetting the coordinates to satisfy the constraints. Its cost is independent of the number of constraints of all internal degrees of freedom. The accuracy of energy conservation is higher than that of the symplectic splitting method in [6] for a single free molecule. For general cases, M-RATTLE achieves the same accuracy for the energy conservation as the symplectic splitting method in [6], but the cost is a little higher than that of the symplectic splitting method since M-RATTLE is semi-implicit.

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