RATTLE Recipe For General Holonomic Constraints: Angle And Torsion Constraints

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The popular RATTLE algorithm for imposing bond-stretch constraints in molecular dynamics simulations is generalized here to handle arbitrary holonomic constraints. In particular, RATTLE expressions are given for the important angle-bend and torsional internal-coordinate constraints. This general formulation of RATTLE combines the computational advantages of the velocity Verlet integration algorithm with the flexibility and computational advantages of using general holonomic constraints.

1 INTRODUCTION

Ryckaert et al. [1] developed the SHAKE algorithm for applying bond-stretch constraints in molecular dynamics (MD) simulations, using the basic Verlet[2] integration algorithm. To avoid the computational drawbacks[3, 4, 5] of the basic Verlet scheme, Andersen[4] used instead the velocity Verlet algorithm[5] to impose bond-stretch constraints, and termed the resulting algorithm RATTLE. Ryckaert[6] later generalized SHAKE to handle arbitrary holonomic constraints. The possibility of imposing general holonomic constraints in MD simulations provides the ability to selectively freeze particular degrees of freedom, without having to interfere with others. As a simple example, to freeze the angle-bend in a triatomic (e.g. water model) using only bond-stretch constraints requires imposing total rigidity on the molecule by means of triangulation[7, 8]. However, freezing the angle-bend can be achieved more directly by imposing a single angle constraint, without constraining any of the bond-stretches. In addition, arbitrary holonomic constraints can offer computational advantages over equivalent pure stretch constraints, as discussed later. In Section 2, RATTLE is generalized to impose arbitrary holonomic constraints in MD simulations, and useful RATTLE expressions for angle-bend and torsional internal-coordinate constraints are given in Section 3.

2 RATTLE For General Holonomic Constraints

Unlike the basic Verlet scheme[2], the velocity Verlet algorithm[5, 9] involves two stages. First, the positions are determined by

$$\mathbf{r}_i(t_0+\delta t) = \mathbf{r}_i(t_0) + [\delta t]\dot{\mathbf{r}}_i(t_0) + \frac{[\delta t]^2}{2m_i}\mathbf{f}_i(t_0) \tag{1}$$

where $\mathbf{f}_i$ is the force on particle i, and then the velocities are computed as

$$\dot{\mathbf{r}}_i(t_0+\delta t) = \dot{\mathbf{r}}_i(t_0) + \frac{[\delta t]}{2m_i}\{\mathbf{f}_i(t_0) + \mathbf{f}_i(t_0+\delta t)\} \tag{2}$$

In the first stage, the positions at time $(t_0+\delta t)$ are calculated from the positions and velocities at time t_0, as given by Eq. (1). With the positions at time $(t_0+\delta t)$ available, the forces at time $(t_0+\delta t)$ can be computed, for use in the second stage, to evaluate the velocities at time $(t_0+\delta t)$ by means of Eq. (2).

Consider a system of N interacting particles subject to l general holonomic constraints

$$\sigma_k(\{\mathbf{r}(t)\}) = 0 \quad (k = 1, \ldots, l) \tag{3}$$

where $\{\mathbf{r}(t)\}$ denotes the coordinates of the subset of n_k particles involved in σ_k. The constrained coordinates are given[1, 6, 10] by

$$\mathbf{r}_i(t_0+\delta t, \{\gamma\}) = \mathbf{r}'_i(t_0+\delta t) - \frac{[\delta t]^2}{2m_i}\sum_{k=1}^{l}\gamma_k[\nabla_i\sigma_k](t_0) \tag{4}$$

The unconstrained coordinates $\mathbf{r}'_i(t_0+\delta t)$ are given by means of Eq. (1) as

$$\mathbf{r}'_i(t_0+\delta t) = \mathbf{r}_i(t_0) + [\delta t]\dot{\mathbf{r}}_i(t_0) + \frac{[\delta t]^2}{2m_i}\mathbf{F}_i(t_0) \tag{5}$$

where $\mathbf{F}_i$ is the potential energy force on particle i. The parameters $\{\gamma\}$ are chosen such that the constrained coordinates at time $(t_0+\delta t)$ satisfy the constraint equations (within a desired tolerance), and either the "matrix method" or the SHAKE procedure can be used[1, 6, 10] to obtain the $\{\gamma\}$. The constrained velocities are given by

$$\dot{\mathbf{r}}_i(t_0+\delta t, \{\eta\}) = \dot{\mathbf{r}}'_i(t_0+\delta t) - \frac{[\delta t]}{2m_i}\sum_{k=1}^{l}\eta_k[\nabla_i\sigma_k](t_0+\delta t) \tag{6}$$

where, using Eq. (2), we have

$$\dot{\mathbf{r}}'_i(t_0+\delta t) = \dot{\mathbf{r}}_i(t_0) + \frac{[\delta t]}{2m_i}\left\{\mathbf{F}_i(t_0) - \sum_{k=1}^{l}\gamma_k[\nabla_i\sigma_k](t_0) + \mathbf{F}_i(t_0+\delta t)\right\} \tag{7}$$

The parameters $\{\eta\}$ are chosen such that the constrained velocities at time $(t_0 + \delta t)$ satisfy the constraint equations, more specifically their time derivatives. Accordingly, differentiating Eq. (3) with respect to time we get

$$\frac{d}{dt}\,\sigma_k\left(\{\mathbf{r}(t_0+\delta t)\}\right) = \sum_{i=1}^{n_k} \dot{\mathbf{r}}_i(t_0+\delta t)\cdot\left[\nabla_i\sigma_k\right]\left(\{\mathbf{r}(t_0+\delta t)\}\right) = 0 \tag{8}$$

where $\dot{\mathbf{r}}_i(t_0+\delta t)$ is inserted from Eq. (6). Again, either numerical matrix inversion or the SHAKE procedure can be used to solve the set of l linear equations Eq. (8) for the $\{\eta\}$. Since solution for the $\{\gamma\}$ and $\{\eta\}$ by matrix techniques becomes computationally expensive for systems with large numbers of coupled constraints, we concentrate here on the solution by the SHAKE procedure, namely RATTLE.

The first of the two stages of the RATTLE formulation for general holonomic constraints, described here, is identical to the generalized SHAKE scheme[6, 10]. The SHAKE algorithm consists of an iterative loop inside which the constraints are considered individually and successively. During an iteration, the algorithm successively selects every constraint and corrects the positions of the subset of particles involved in that constraint, to satisfy it. Consider a certain iteration and a particular constraint σ_k. Let $\left\{\mathbf{r}^{old}(t_0+\delta t)\right\}$ be the subset of n_k particle positions involved in σ_k, with values including all changes up to this point in the iteration. The new positions of the particles $\{\mathbf{r}^{new}(t_0+\delta t)\}$ obtained in the current iteration are computed as

$$\mathbf{r}_i^{new}(t_0+\delta t) = \mathbf{r}_i^{old}(t_0+\delta t) - \frac{[\delta t]^2}{2m_i}\gamma_k^{new}[\nabla_i\sigma_k](t_0) \quad (i=1,\ldots,n_k) \tag{9}$$

where the starting value of $\mathbf{r}_i^{old}(t_0+\delta t)$ is given by Eq. (5). These new positions should satisfy the constraint equation for σ_k, leading to

$$\sigma_k\left(\{\mathbf{r}^{new}(t_0+\delta t)\}\right) = \sigma_k\left(\left\{\mathbf{r}^{old}(t_0+\delta t)\right\} - \left\{\frac{[\delta t]^2}{2m}\gamma_k^{new}[\nabla\sigma_k](t_0)\right\}\right) = 0 \tag{10}$$

Equation (10) is usually nonlinear in γ_k^{new}, even for a bond-stretch constraint. Taylor expanding $\sigma_k\left(\{\mathbf{r}^{new}(t_0+\delta t)\}\right)$ about $\left\{\mathbf{r}^{old}(t_0+\delta t)\right\}$, Eq. (10) becomes

$$\begin{aligned}&\sigma_k\left(\left\{\mathbf{r}^{old}(t_0+\delta t)\right\} - \left\{\frac{[\delta t]^2}{2m}\gamma_k^{new}[\nabla\sigma_k](t_0)\right\}\right) = \\ &\sigma_k\left(\left\{\mathbf{r}^{old}(t_0+\delta t)\right\}\right) - \sum_{i=1}^{n_k}\frac{[\delta t]^2}{2m_i}\gamma_k^{new}[\nabla_i\sigma_k](t_0)\cdot\left[\nabla_i\sigma_k\right]\left(\left\{\mathbf{r}^{old}(t_0+\delta t)\right\}\right) + \ldots = 0\end{aligned} \tag{11}$$

where the nonlinear terms are not shown explicitly. For computational efficiency, all terms higher than first order in Eq. (11) are usually neglected, the iterative process over constraints ensuring

the resulting solution satisfies Eq. (11). From Eq. (11) one gets

$$\gamma_k^{new} = [\delta t]^{-2} \frac{\sigma_k\left(\left\{\mathbf{r}^{old}(t_0+\delta t)\right\}\right)}{\sum_{i=1}^{n_k}(1/2m_i)[\nabla_i\sigma_k](t_0)\cdot[\nabla_i\sigma_k]\left(\{\mathbf{r}^{old}(t_0+\delta t)\}\right)} \tag{12}$$

Exactly as with SHAKE, iterations over the general holonomic constraints continue until all are satisfied, within some tolerance. When all constraints have been satisfied and the constrained coordinates at $(t_0+\delta t)$ are available, the potential energy forces $\{\mathbf{F}(t_0+\delta t)\}$ are computed for use in the following second stage of the generalized RATTLE.

During an iteration of this second stage, the algorithm again successively selects every constraint and corrects the velocities of the subset of particles involved in that constraint, to satisfy its time derivative. Considering again some iteration and a particular constraint σ_k, the new velocities of the particles $\{\dot{\mathbf{r}}^{new}(t_0+\delta t)\}$ obtained in the current iteration are given by

$$\dot{\mathbf{r}}_i^{new}(t_0+\delta t) = \dot{\mathbf{r}}_i^{old}(t_0+\delta t) - \frac{[\delta t]}{2m_i}\eta_k^{new}[\nabla_i\sigma_k](t_0+\delta t) \quad (i=1,\ldots,n_k) \tag{13}$$

where the starting value of $\dot{\mathbf{r}}_i^{old}(t_0+\delta t)$ is given by Eq. (7). These new velocities should satisfy the time derivative of the constraint equation. Accordingly, inserting Eq. (13) into Eq. (8) and solving the resulting linear equation for η_k^{new} gives

$$\eta_k^{new} = [\delta t]^{-1} \frac{\sum_{i=1}^{n_k}\dot{\mathbf{r}}_i^{old}(t_0+\delta t)\cdot[\nabla_i\sigma_k]\left(\{\mathbf{r}(t_0+\delta t)\}\right)}{\sum_{i=1}^{n_k}(1/2m_i)[\nabla_i\sigma_k]\left(\{\mathbf{r}(t_0+\delta t)\}\right)\cdot[\nabla_i\sigma_k]\left(\{\mathbf{r}(t_0+\delta t)\}\right)} \tag{14}$$

As with the first stage of RATTLE, iteration over constraints continues until all the constraints on the velocities have been satisfied within a selected tolerance. The entire RATTLE procedure is then repeated at the next time MD step.

3 RATTLE With Internal-Coordinate Constraints

The above general formulation of RATTLE is specialized here to angle-bend and torsional constraints, with the bond-stretch constraints case reviewed merely for completeness. Consider the l general holonomic constraints Eq. (3) as comprising l_s bond-stretch constraints, l_a bond-angle constraints, and l_t torsional constraints. For bond-stretch constraints Eq. (3) takes the form

$$\sigma_k(\{\mathbf{r}\}) = [\mathbf{r}_j(t)-\mathbf{r}_i(t)]^2 - d_{ij}^2 = 0 \quad (k=1,\ldots,l_s) \tag{15}$$

where i and j are the two particles involved in the particular constraint σ_k, and d_{ij} is the constant distance between them. For the first stage of RATTLE, inserting $\sigma_k(\{\mathbf{r}\})$ of Eq. (15) into Eq. (9) yields

$$\begin{aligned}
\mathbf{r}_j^{new}(t_0+\delta t) &= \mathbf{r}_j^{old}(t_0+\delta t) - \frac{1}{m_j}[\delta t]^2\gamma_k^{new}[\mathbf{r}_j(t_0)-\mathbf{r}_i(t_0)] \\
\mathbf{r}_i^{new}(t_0+\delta t) &= \mathbf{r}_i^{old}(t_0+\delta t) - \frac{1}{m_i}[\delta t]^2\gamma_k^{new}[\mathbf{r}_i(t_0)-\mathbf{r}_j(t_0)]
\end{aligned} \tag{16}$$

and Eq. (12) reduces to

$$\gamma_k^{new} = [\delta t]^{-2} \frac{[\mathbf{r}_j^{old}(t_0+\delta t) - \mathbf{r}_i^{old}(t_0+\delta t)]^2 - d_{ij}^2}{2[(1/m_i)+(1/m_j)][\mathbf{r}_j(t_0) - \mathbf{r}_i(t_0)] \cdot [\mathbf{r}_j^{old}(t_0+\delta t) - \mathbf{r}_i^{old}(t_0+\delta t)]} \quad (k = 1, \ldots, l_s) \tag{17}$$

In the second stage Eq. (13) becomes

$$\begin{aligned} \dot{\mathbf{r}}_j^{new}(t_0+\delta t) &= \dot{\mathbf{r}}_j^{old}(t_0+\delta t) - \frac{1}{m_j}[\delta t]\eta_k^{new}[\mathbf{r}_j(t_0+\delta t) - \mathbf{r}_i(t_0+\delta t)] \\ \dot{\mathbf{r}}_i^{new}(t_0+\delta t) &= \dot{\mathbf{r}}_i^{old}(t_0+\delta t) - \frac{1}{m_i}[\delta t]\eta_k^{new}[\mathbf{r}_i(t_0+\delta t) - \mathbf{r}_j(t_0+\delta t)] \end{aligned} \tag{18}$$

and Eq. (14) reduces to

$$\eta_k^{new} = [\delta t]^{-1} \frac{[\mathbf{r}_j(t_0+\delta t) - \mathbf{r}_i(t_0+\delta t)][\dot{\mathbf{r}}_j^{old}(t_0+\delta t) - \dot{\mathbf{r}}_i^{old}(t_0+\delta t)]}{[(1/m_i)+(1/m_j)][\mathbf{r}_j(t_0+\delta t) - \mathbf{r}_i(t_0+\delta t)]^2} \quad (k = 1, \ldots, l_s) \tag{19}$$

Because the constrained coordinates at $(t_0 + \delta t)$, from the first stage, satisfy (within a given tolerance) the constraint Eq. (15), Eq. (19) can be rewritten as

$$\eta_k^{new} = [\delta t]^{-1} \frac{[\mathbf{r}_j(t_0+\delta t) - \mathbf{r}_i(t_0+\delta t)][\dot{\mathbf{r}}_j^{old}(t_0+\delta t) - \dot{\mathbf{r}}_i^{old}(t_0+\delta t)]}{[(1/m_i)+(1/m_j)]\, d_{ij}^2} \quad (k = 1, \ldots, l_s) \tag{20}$$

We have recovered in Eqs. (16), (17), (18), and (20) the usual RATTLE expressions[4]. For bond-angle constraints Eq. (3) takes the form

$$\sigma_k(\{\mathbf{r}\}) = \phi_{abc}(\{\mathbf{r}\}) - \alpha_{abc} = 0 \quad (k = 1, \ldots, l_a) \tag{21}$$

where a, b and c are the three particles involved in the particular constraint σ_k, $\phi_{abc} \equiv \arccos(\hat{\mathbf{r}}_{ab} \cdot \hat{\mathbf{r}}_{cb})$ is the angle at b formed by the (abc) triplet of particles, $\hat{\mathbf{r}}_{ab} \equiv \mathbf{r}_{ab}/|\mathbf{r}_{ab}|$, $\mathbf{r}_{ab} \equiv \mathbf{r}_a - \mathbf{r}_b$, and α_{abc} is the constant angle-bend value. For the first stage of the generalized RATTLE, inserting the constraint $\sigma_k(\{\mathbf{r}\})$ of Eq. (21) into Eq. (9) gives

$$\mathbf{r}_i^{new}(t_0+\delta t) = \mathbf{r}_i^{old}(t_0+\delta t) - \frac{[\delta t]^2}{2m_i}\gamma_k^{new}[\nabla_i \phi_{abc}](t_0) \quad (i = a, b, c) \tag{22}$$

and Eq. (12) reduces to

$$\gamma_k^{new} = [\delta t]^{-2} \frac{\phi_{abc}\left(\left\{\mathbf{r}^{old}(t_0+\delta t)\right\}\right) - \alpha_{abc}}{\sum_{i=1}^{n_k}(1/2m_i)[\nabla_i \phi_{abc}](t_0) \cdot [\nabla_i \phi_{abc}](\{\mathbf{r}^{old}(t_0+\delta t)\})} \quad (k = 1, \ldots, l_a) \tag{23}$$

For the second stage, Eq. (13) becomes

$$\dot{\mathbf{r}}_i^{new}(t_0+\delta t) = \dot{\mathbf{r}}_i^{old}(t_0+\delta t) - \frac{[\delta t]}{2m_i}\eta_k^{new}[\nabla_i \phi_{abc}](\{\mathbf{r}(t_0+\delta t)) \quad (i = a, b, c) \tag{24}$$

and Eq. (14) reduces to

$$\eta_k^{new} = [\delta t]^{-1} \frac{\sum_{i=1}^{n_k} \dot{\mathbf{r}}_i^{old}(t_0+\delta t) \cdot [\nabla_i \phi_{abc}]\left(\{\mathbf{r}(t_0+\delta t)\}\right)}{\sum_{i=1}^{n_k} (1/2m_i) \left\{[\nabla_i \phi_{abc}]\left(\{\mathbf{r}(t_0+\delta t)\}\right)\right\}^2} \quad (k = 1, \ldots, l_a) \tag{25}$$

Note that the expressions for $\nabla_i \phi_{abc}$ in Eqs. (22)-(25) are immediately available from the Wilson vectors[11] for the angle-bend internal coordinate. Finally, for torsional constraints Eq. (3) takes the form

$$\sigma_k(\{\mathbf{r}\}) = \tau_{abcd}(\{\mathbf{r}\}) - \beta_{abcd} = 0 \quad (k = 1, \ldots, l_t) \tag{26}$$

where a, b, c, and d are the four particles involved in the particular constraint σ_k, and

$$\tau_{abcd} \equiv \arccos\left[\frac{(\hat{\mathbf{r}}_{ab} \times \hat{\mathbf{r}}_{cb}) \cdot (\hat{\mathbf{r}}_{bc} \times \hat{\mathbf{r}}_{dc})}{\sin\phi_{abc}\ \sin\phi_{bcd}}\right] \tag{27}$$

is the dihedral angle formed by the $(abcd)$ quadruplet of particles with constraint value β_{abcd}. For the first stage of the generalized RATTLE, inserting $\sigma_k(\{\mathbf{r}\})$ of Eq. (26) into Eq. (9) yields

$$\mathbf{r}_i^{new}(t_0+\delta t) = \mathbf{r}_i^{old}(t_0+\delta t) - \frac{[\delta t]^2}{2m_i} \gamma_k^{new} [\nabla_i \tau_{abcd}](t_0) \quad (i = a, b, c, d) \tag{28}$$

and Eq. (12) reduces to

$$\gamma_k^{new} = [\delta t]^{-2} \frac{\tau_{abcd}\left(\left\{\mathbf{r}^{old}(t_0+\delta t)\right\}\right) - \beta_{abcd}}{\sum_{i=1}^{n_k} (1/2m_i)[\nabla_i \tau_{abcd}](t_0) \cdot [\nabla_i \tau_{abcd}](\{\mathbf{r}^{old}(t_0+\delta t)\})} \quad (k = 1, \ldots, l_t) \tag{29}$$

In the second stage, Eq. (13) becomes

$$\dot{\mathbf{r}}_i^{new}(t_0+\delta t) = \dot{\mathbf{r}}_i^{old}(t_0+\delta t) - \frac{[\delta t]}{2m_i} \eta_k^{new} [\nabla_i \tau_{abc}](\{\mathbf{r}(t_0+\delta t)) \quad (i = a, b, c, d) \tag{30}$$

and Eq. (14) reduces to

$$\eta_k^{new} = [\delta t]^{-1} \frac{\sum_{i=1}^{n_k} \dot{\mathbf{r}}_i^{old}(t_0+\delta t) \cdot [\nabla_i \tau_{abc}]\left(\{\mathbf{r}(t_0+\delta t)\}\right)}{\sum_{i=1}^{n_k} (1/2m_i) \left\{[\nabla_i \tau_{abc}]\left(\{\mathbf{r}(t_0+\delta t)\}\right)\right\}^2} \quad (k = 1, \ldots, l_t) \tag{31}$$

Again, the expressions for $\nabla_i \tau_{abcd}$ in Eqs. (28)-(31) are available from the Wilson vectors[11] for the torsional internal coordinate.

CONCLUSION

A formulation of RATTLE for imposing general holonomic constraints in MD simulations was described, and expressions for angle-bend and torsional constraints were given. In MD simulations of

systems involving constraints, the computation of the constraint forces typically takes far less CPU time than the computation of the forces deriving from the potential energy of the system. As larger systems with constraints are considered, or molecular models involving larger sets of constraints are simulated, the computation of constraint forces becomes increasingly CPU intensive[12, 13] and can parallel in computational cost[14, 15] the evaluation of the potential energy forces. To deal with this problem, various approaches[15, 10] have been developed for improving the efficiency of computing the constraint forces in MD simulations. One suggested strategy calls for the use of equivalent alternative constraints. A case in point is the substantial improvement in efficiency that results when angle-bend constraints are used[10] in place of the slowly converging triangulation procedure[7, 8] for imposing angle constraints. The formulation of RATTLE for general holonomic constraints, given in this article, combines these computational advantages of arbitrary forms of holonomic constraints with those of the velocity Verlet algorithm.

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