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Modified Potential Energy Functions for Constrained Molecular Dynamics

Preprint SC 97-49 (December 1997)

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13th March 1998

Abstract

In molecular dynamics the highly oscillatory vibrations in the chemical bonds are often replaced by holonomic constraints that freeze the bond length/angle to its equilibrium value. In some cases this approach can be justified if the force constants of the bond vibrations are sufficiently large. However, for moderate values of the force constant, the constrained system might lead to a dynamical behavior that is too "rigid" compared to the flexible model. To compensate for this effect, the concept of soft constraints was introduced in [7],[12],[13]. However, its implementation is rather expensive. In this paper, we suggest an alternative approach that modifies the force field instead of the constraint functions. This leads to a more efficient method that avoids the resonance induced instabilities of multiple-time-stepping [5] and the above described effect of standard constrained dynamics.

1 Introduction

Classical molecular dynamics [1] leads to Hamiltonian equations of motion of type

$$\begin{aligned} \frac{d}{dt}\boldsymbol{q} &= \boldsymbol{M}^{-1}\boldsymbol{p}\,, \\ \frac{d}{dt}\boldsymbol{p} &= -\boldsymbol{\nabla}_{\boldsymbol{q}} U(\boldsymbol{q})\,, \end{aligned}$$

$\boldsymbol{q},\boldsymbol{p} \in R^{3N}$, $\boldsymbol{M} \in R^{3N\times 3N}$ a symmetric, positive-definite mass matrix, and $U : R^{3N} \to R$ a potential energy function. The Hamiltonian (energy) of this system is

$$H(\boldsymbol{q},\boldsymbol{p}) = \frac{\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{p}}{2} + U(\boldsymbol{q})$$

which is a constant of motion.

In many cases, the potential energy function U can be split into a part U_b describing the bond stretching and bond angle bending modes, i.e.

$$U_b(\boldsymbol{q}) := \sum_{i=1}^{m} \frac{K_i}{2} g_i(\boldsymbol{q})^2$$

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with $K_i \gg 1$ a force constant and $g_i : R^{3N} \to R$ an appropriate function, $i = 1, \ldots, m$, and a remaining part U_l containing the Lennard-Jones and electrostatic interactions. Using a more compact notation, we write

$$U_b(\boldsymbol{q}) \;=\; \frac{1}{2}\boldsymbol{g}(\boldsymbol{q})^T \boldsymbol{K}\boldsymbol{g}(\boldsymbol{q})\,,$$

$\boldsymbol{K} \in R^{m\times m}$ the diagonal matrix with entries $k_{ii} = K_i$ and $\boldsymbol{g} : R^{3N} \to R^m$, $\boldsymbol{g} = (g_1, \ldots, g_m)^T$. The corresponding equations of motion are[1]

$$\begin{aligned}
\frac{d}{dt}\boldsymbol{q} &= \boldsymbol{M}^{-1}\boldsymbol{p}\,,\\
\frac{d}{dt}\boldsymbol{p} &= -\boldsymbol{\nabla}_{\boldsymbol{q}} U(\boldsymbol{q}) \;=\; -\boldsymbol{\nabla}_{\boldsymbol{q}} U_l(\boldsymbol{q}) - \boldsymbol{\nabla}_{\boldsymbol{q}}\boldsymbol{g}(\boldsymbol{q})\boldsymbol{K}\boldsymbol{g}(\boldsymbol{q})
\end{aligned}$$

which can be discretized by the well-known Verlet method [17], i.e.

$$\begin{aligned}
\boldsymbol{q}_{n+1} &= \boldsymbol{q}_n + \Delta t \boldsymbol{M}^{-1}\boldsymbol{p}_{n+1/2}\,,\\
\boldsymbol{p}_{n+1/2} &= \boldsymbol{p}_n - \frac{\Delta t}{2}\boldsymbol{\nabla}_{\boldsymbol{q}} U(\boldsymbol{q}_n)\,,\\
\boldsymbol{p}_{n+1} &= \boldsymbol{p}_{n+1/2} - \frac{\Delta t}{2}\boldsymbol{\nabla}_{\boldsymbol{q}} U(\boldsymbol{q}_{n+1})\,.
\end{aligned}$$

However, if $K_i \gg 1$, a small step-size Δt of order ϵ with

$$\epsilon^{-2} \;=\; \max_{i=1,\ldots,m} K_i\,,$$

has to be used. This problem can be avoided by either using multiple-time-stepping methods [8],[16],[4] or by replacing the bond stretching and bond angle bending modes by holonomic constraints [1] which leads to the constrained Hamiltonian system

$$\frac{d}{dt}\boldsymbol{q} \;=\; \boldsymbol{M}^{-1}\boldsymbol{p}\,, \tag{1}$$

$$\frac{d}{dt}\boldsymbol{p} \;=\; -\boldsymbol{\nabla}_{\boldsymbol{q}} U(\boldsymbol{q}) - \boldsymbol{\nabla}_{\boldsymbol{q}}\boldsymbol{g}(\boldsymbol{q})\boldsymbol{\lambda}\,, \tag{2}$$

$$\boldsymbol{0} \;=\; \boldsymbol{g}(\boldsymbol{q}) \tag{3}$$

on the constraint manifold

$$\mathcal{M} = \{(\boldsymbol{q}, \boldsymbol{p}) \in R^{6N} : \boldsymbol{g}(\boldsymbol{q}) = \boldsymbol{0}\,, \quad \boldsymbol{\partial}_{\boldsymbol{q}}\boldsymbol{g}(\boldsymbol{q})\boldsymbol{M}^{-1}\boldsymbol{p} = \boldsymbol{0}\}$$

with Hamiltonian

$$H(\boldsymbol{q}, \boldsymbol{p}) = \frac{\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{p}}{2} + U(\boldsymbol{q}) + \boldsymbol{g}(\boldsymbol{q})^T\boldsymbol{\lambda}\,.$$

The vector of Lagrange multipliers $\boldsymbol{\lambda} \in R^m$ is determined by the constraints $\boldsymbol{g}(\boldsymbol{q}) = \boldsymbol{0}$. The constrained system (1)-(3) can be discretized by the symplectic

[1] The Jacobian of $\boldsymbol{g}$ at $\boldsymbol{q}$ is denoted by $\boldsymbol{\partial}_{\boldsymbol{q}}\boldsymbol{g}(\boldsymbol{q}) \in R^{m\times 3N}$. Its transpose, the gradient, is denoted by $\boldsymbol{\nabla}_{\boldsymbol{q}}\boldsymbol{g}(\boldsymbol{q}) = [\boldsymbol{\partial}_{\boldsymbol{q}}\boldsymbol{g}(\boldsymbol{q})]^T$.

SHAKE or RATTLE method [10], i.e.

$$
\begin{aligned}
\boldsymbol{q}_{n+1} &= \boldsymbol{q}_n + \Delta t \boldsymbol{M}^{-1} \boldsymbol{p}_{n+1/2}\,, \\
\boldsymbol{p}_{n+1/2} &= \boldsymbol{p}_n - \frac{\Delta t}{2} \boldsymbol{\nabla}_{\boldsymbol{q}} U(\boldsymbol{q}_n) - \frac{\Delta t}{2} \boldsymbol{\nabla}_{\boldsymbol{q}} \boldsymbol{g}(\boldsymbol{q}_n) \boldsymbol{\lambda_n}\,, \\
\boldsymbol{0} &= \boldsymbol{g}(\boldsymbol{q}_{n+1})\,, \\
\boldsymbol{p}_{n+1} &= \boldsymbol{p}_{n+1/2} - \frac{\Delta t}{2} \boldsymbol{\nabla}_{\boldsymbol{q}} U(\boldsymbol{q}_{n+1}) - \frac{\Delta t}{2} \boldsymbol{\nabla}_{\boldsymbol{q}} \boldsymbol{g}(\boldsymbol{q}_{n+1}) \boldsymbol{\mu_n}\,, \\
\boldsymbol{0} &= \boldsymbol{\partial}_{\boldsymbol{q}} \boldsymbol{q}(\boldsymbol{q}_{n+1}) \boldsymbol{M}^{-1} \boldsymbol{p}_{n+1}\,.
\end{aligned}
$$

The transition from a flexible model to a constrained system requires justification. Let us assume that the matrix $\boldsymbol{\partial}_{\boldsymbol{q}} \boldsymbol{g}(\boldsymbol{q}) \boldsymbol{M}^{-1} \boldsymbol{\nabla}_{\boldsymbol{q}} \boldsymbol{g}(\boldsymbol{q})$ is constant for all $\boldsymbol{q}$ satisfying the holonomic constraint $\boldsymbol{g}(\boldsymbol{q}) = \boldsymbol{0}$. Then the following results can be shown[2] [2],[14] provided the constants $K_i \gg 1$, $i = 1, \ldots, m$, are sufficiently large:

(i) The total energy in the bond stretching and bond angle bending modes is almost constant over exponentially long periods of time[3].

(ii) The flexible model reduces to the constrained system in the limit $K_i \to \infty$, $i = 1, \ldots, m$.

According to (ii), the constrained dynamics is valid in the limit of sufficiently large force constants K_i. In typical molecular systems, like water, this assumption is not necessarily satisfied and one observes that the constrained model is too rigid compared to the flexible dynamics. In fact, one easily verifies by numerical simulation that the flexible dynamics leads to fast oscillations about the minimum of the total potential energy U along the bond stretching and bond angle bending modes. This minimum is approximated by the holonomic constraint $\boldsymbol{g}(\boldsymbol{q}) = \boldsymbol{0}$ only up to terms of size $1/K_i$, $i = 1, \ldots, m$. A better approximation is obtained by using the following approximation of the minimum of the total potential energy U along $\boldsymbol{r} = \boldsymbol{g}(\boldsymbol{q})$:

$$
\boldsymbol{\nabla}_{\boldsymbol{r}} U(\boldsymbol{q}) \approx \tilde{\boldsymbol{g}}(\boldsymbol{q}) = \boldsymbol{0}
$$

with the modified constraint function

$$
\tilde{\boldsymbol{g}}(\boldsymbol{q}) := \boldsymbol{\partial}_{\boldsymbol{q}} \boldsymbol{g}(\boldsymbol{q}) \boldsymbol{M}^{-1} \boldsymbol{\nabla}_{\boldsymbol{q}} U(\boldsymbol{q}) = \boldsymbol{\partial}_{\boldsymbol{q}} \boldsymbol{g}(\boldsymbol{q}) \boldsymbol{M}^{-1} \left[\boldsymbol{\nabla}_{\boldsymbol{q}} U_l(\boldsymbol{q}) + \boldsymbol{\nabla}_{\boldsymbol{q}} \boldsymbol{g}(\boldsymbol{q}) \boldsymbol{K} \boldsymbol{g}(\boldsymbol{q}) \right]. \tag{4}
$$

This gives rise to the constrained Hamiltonian system

$$
\begin{aligned}
\frac{d}{dt} \boldsymbol{q} &= \boldsymbol{M}^{-1} \boldsymbol{p}\,, && (5) \\
\frac{d}{dt} \boldsymbol{p} &= -\boldsymbol{\nabla}_{\boldsymbol{q}} U(\boldsymbol{q}) - \boldsymbol{\nabla}_{\boldsymbol{q}} \tilde{\boldsymbol{g}}(\boldsymbol{q}) \boldsymbol{\lambda}\,, && (6) \\
\boldsymbol{0} &= \tilde{\boldsymbol{g}}(\boldsymbol{q}) && (7)
\end{aligned}
$$

[2] These results do not hold if $\boldsymbol{\partial}_{\boldsymbol{q}} \boldsymbol{g}(\boldsymbol{q}) \boldsymbol{M}^{-1} \boldsymbol{\nabla}_{\boldsymbol{q}} \boldsymbol{g}(\boldsymbol{q})$ is not constant [15],[9].

[3] Exponentially long periods of time means that the energy is almost conserved over a time period T proportional to $e^{\gamma\kappa}$, $\gamma > 0$ an appropriate constant and $\kappa^{2m} = \min_{i=1,\ldots m} K_i$.

on the modified constraint manifold

$$\widetilde{\mathcal{M}} = \{(\boldsymbol{q},\boldsymbol{p}) \in R^{6N} : \tilde{\boldsymbol{g}}(\boldsymbol{q}) = \boldsymbol{0}\,, \quad \boldsymbol{\partial_q}\tilde{\boldsymbol{g}}(\boldsymbol{q})\boldsymbol{M}^{-1}\boldsymbol{p} = \boldsymbol{0}\}$$

with Hamiltonian

$$\widetilde{H}(\boldsymbol{q},\boldsymbol{p}) = \frac{\boldsymbol{p}^T\boldsymbol{M}^{-1}\boldsymbol{p}}{2} + U(\boldsymbol{q}) + \tilde{\boldsymbol{g}}(\boldsymbol{q})^T\boldsymbol{\lambda}\,.$$

The modified equations of motion can still be discretized by the SHAKE or RATTLE method. This approach was suggested in [7],[12],[13]. Note that the evaluation of $\tilde{\boldsymbol{g}}$ requires the computation of the long-range force field $-\boldsymbol{\nabla_q}U_l$. This is in contrast to standard constrained dynamics and implies additional long-range force field evaluations per time step. However, noting that the only significant contributions to the modified constraint function $\tilde{\boldsymbol{g}}$ come from nearest neighborhood interactions, the potential energy U_l can be split as in multiple-time-stepping methods [8],[16],[4] and only the nearest neighborhood interactions are included in the definition (4) of $\tilde{\boldsymbol{g}}$. In fact, the main disadvantage of the formulation lies in the fact that it requires the computation of the gradient of $\tilde{\boldsymbol{g}}$ and thus the computation of the Hessian of U.

2 A Modified Potential Energy Function

As already pointed out, the approximation of a flexible system by the constrained Hamiltonian system (1)-(3) neglects contributions of size $1/K_i$, $i = 1,\ldots,m$, [12]. The idea of soft constraints is to partially include those terms ([7],[12],[13]). However, the modified constraint functions are costly to implement. Here we suggest a different approach. Instead of modifying the constraint functions we modify the potential energy function U.

The basic idea is as follows: We define a symplectic change of coordinates [11]

$$(\boldsymbol{q},\boldsymbol{p}) = \boldsymbol{\psi}(\boldsymbol{Q},\boldsymbol{P}) \tag{8}$$

such that $\boldsymbol{\psi}$ maps the constraint manifold $\mathcal{M}$ onto the modified constraint manifold $\widetilde{\mathcal{M}}$. This allows us to pull the modified constrained system (5)-(7) back to a system on $\mathcal{M}$ with modified Hamiltonian

$$\widehat{H}(\boldsymbol{Q},\boldsymbol{P}) \;:=\; \widetilde{H}(\boldsymbol{\psi}(\boldsymbol{Q},\boldsymbol{P}))\,, \tag{9}$$

$(\boldsymbol{Q},\boldsymbol{P}) \in \mathcal{M}$ [11]. The corresponding equations of motion on $\mathcal{M}$ have solutions that can be identified with the solutions of (5)-(7) by means of the symplectic change of coordinates (8).

Let us now define such a coordinate transformation. For that reason, we first introduce the transformation

$$\boldsymbol{q} \;:=\; \phi(\boldsymbol{Q})$$

by means of

$$\begin{aligned} \boldsymbol{q} \;&:=\; \boldsymbol{Q} + \boldsymbol{M}^{-1}\,\boldsymbol{\nabla_Q}\boldsymbol{g}(\boldsymbol{Q})\,\boldsymbol{\eta}\,, \\ \boldsymbol{0} \;&=\; \boldsymbol{\partial_q}\boldsymbol{g}(\boldsymbol{q})\,\boldsymbol{M}^{-1}\,\boldsymbol{\nabla_q}U(\boldsymbol{q}) \;=\; \tilde{\boldsymbol{g}}(\boldsymbol{q}) \end{aligned} \tag{10}$$

with $\boldsymbol{g}(\boldsymbol{Q}) = \boldsymbol{0}$. The resulting nonlinear system in the variable $\boldsymbol{\eta} \in R^m$ can be solved by Newton's method with the simplified (symmetric) Jacobian[4]

$$\boldsymbol{J} = [\boldsymbol{\partial_Q g}(\boldsymbol{Q})\boldsymbol{M}^{-1}\boldsymbol{\nabla_Q g}(\boldsymbol{Q})]\,\boldsymbol{K}\,[\boldsymbol{\partial_Q g}(\boldsymbol{Q})\boldsymbol{M}^{-1}\boldsymbol{\nabla_Q g}(\boldsymbol{Q})]\,.$$

According to the definition of a symplectic point transformation [11], the corresponding transformation of the momenta is given by [5]

$$[\boldsymbol{\partial_Q \phi}(\boldsymbol{Q})]^T \boldsymbol{p} = \boldsymbol{P}\,.$$

Thus the modified Hamiltonian (9) becomes

$$\widehat{H}(\boldsymbol{Q},\boldsymbol{P}) = \frac{\boldsymbol{P}^T \widehat{\boldsymbol{M}}(\boldsymbol{Q})^{-1}\boldsymbol{P}}{2} + W(\boldsymbol{Q}) + \boldsymbol{g}(\boldsymbol{Q})^T \boldsymbol{\lambda}$$

with modified mass matrix

$$\widehat{\boldsymbol{M}}(\boldsymbol{Q})^{-1} := [\boldsymbol{\partial_Q \phi}(\boldsymbol{Q})]^{-1}\boldsymbol{M}^{-1}[\boldsymbol{\partial_Q \phi}(\boldsymbol{Q})]^{-T}$$

and modified potential energy function

$$\begin{aligned} W(\boldsymbol{Q}) &:= U(\boldsymbol{\phi}(\boldsymbol{Q}))\,, \\ &= U_l(\boldsymbol{q}) + \frac{1}{2}\boldsymbol{g}(\boldsymbol{q})^T \boldsymbol{K}\boldsymbol{g}(\boldsymbol{q})\,. \end{aligned}$$

In the sequel, we assume that the kinematic properties of the body defined by the soft constraints $\tilde{\boldsymbol{g}}(\boldsymbol{q}) = \boldsymbol{0}$ are basically the same as for the body defined by the constraint $\boldsymbol{g}(\boldsymbol{q}) = \boldsymbol{0}$. In other words $\widehat{\boldsymbol{M}}(\boldsymbol{Q}) \approx \boldsymbol{M}$.[6] Thus we obtain the simplified Hamiltonian

$$\widehat{H}(\boldsymbol{Q},\boldsymbol{P}) = \frac{\boldsymbol{P}^T \boldsymbol{M}^{-1}\boldsymbol{P}}{2} + W(\boldsymbol{Q}) + \boldsymbol{g}(\boldsymbol{Q})^T \boldsymbol{\lambda}$$

with corresponding equations of motion

$$\begin{aligned} \frac{d}{dt}\boldsymbol{Q} &= \boldsymbol{M}^{-1}\boldsymbol{P}\,, && (11) \\ \frac{d}{dt}\boldsymbol{P} &= -\boldsymbol{\nabla_Q} W(\boldsymbol{Q}) - \boldsymbol{\nabla_Q g}(\boldsymbol{Q})\boldsymbol{\lambda}\,, && (12) \\ \boldsymbol{0} &= \boldsymbol{g}(\boldsymbol{Q})\,. && (13) \end{aligned}$$

These equations can again be discretized by the SHAKE or RATTLE method. The trick is to keep the evaluation of the gradient

$$\boldsymbol{\nabla_Q} W(\boldsymbol{Q}) \;=\; [\boldsymbol{\partial_Q \phi}(\boldsymbol{Q})]^T \boldsymbol{\nabla_q} U(\boldsymbol{q})$$

cheap. For that reason (10) is modified to

$$\boldsymbol{0} \;=\; \boldsymbol{\partial_Q g}(\boldsymbol{Q})\,\boldsymbol{M}^{-1}\,\boldsymbol{\nabla_q} U(\boldsymbol{q})\,.$$

[4]By our assumption, this matrix is constant on the constraint manifold defined by $\boldsymbol{g}(\boldsymbol{Q}) = \boldsymbol{0}$.

[5]Strictly speaking, the resulting symplectic change of coordinates (8) maps $\mathcal{M}$ into $\widetilde{\mathcal{M}}$ only if the mass matrix $\boldsymbol{M}$ is the identity. This problem can be avoided by an appropriate scaling of the coordinates $\boldsymbol{q}$ and the momenta $\boldsymbol{p}$. However, for simplicity, we skip this technical detail.

[6]This assumption is reasonable since $\boldsymbol{\phi}$ is close to the identity and a slight rearrangement of the particles will not change the kinematic properties in a significant way.

We still denote the corresponding transformation by $\boldsymbol{\phi}$. It is now indeed easily checked that the evaluation of the gradient does no longer require the computation of the Hessian of U_l but only needs the computation of the second derivative of $\boldsymbol{g}$. In other words

$$\begin{aligned} \boldsymbol{dq} &:= \boldsymbol{\partial_Q \phi(Q)\, dQ}\,, \\ &= \boldsymbol{dQ} + \boldsymbol{M}^{-1}\, \boldsymbol{\nabla_Q g(Q)\, d\eta} + \boldsymbol{M}^{-1} \sum_{i=1}^{m} \eta_i\, \boldsymbol{\partial^2_Q} g_i(\boldsymbol{Q})\, \boldsymbol{dQ}\,, \end{aligned}$$

but $\boldsymbol{d\eta}$ is not needed because of

$$\boldsymbol{\partial_Q g(Q)}\, \boldsymbol{M}^{-1}\, \boldsymbol{\nabla_q} U(\boldsymbol{q}) \quad = \quad \boldsymbol{0}\,.$$

Thus the gradient of the modified potential energy W is given by

$$\boldsymbol{\nabla_Q} W(\boldsymbol{Q}) = \left[\boldsymbol{I} + \sum_{i=1}^{m} \eta_i \boldsymbol{\partial^2_Q} g_i(\boldsymbol{Q}) \boldsymbol{M}^{-1}\right] \boldsymbol{\nabla_q} U(\boldsymbol{q})\,.$$

This leads to the following modified constrained discretization:

RATTLE Algorithm with Modified Force Field

Step 1.

$$\begin{aligned} \boldsymbol{q}_n &= \boldsymbol{\phi}(\boldsymbol{Q}_n)\,, \\ \boldsymbol{F}_n &= -[\boldsymbol{\partial_Q \phi}(\boldsymbol{Q}_n)]^T\, \boldsymbol{\nabla_q} U(\boldsymbol{q}_n)\,. \end{aligned}$$

Step 2.

$$\begin{aligned} \boldsymbol{Q}_{n+1} &= \boldsymbol{Q}_n + \Delta t \boldsymbol{M}^{-1} \boldsymbol{P}_{n+1/2}\,, \\ \boldsymbol{P}_{n+1/2} &= \boldsymbol{P}_n + \frac{\Delta t}{2}\left[\boldsymbol{F}_n - \boldsymbol{\nabla_Q g}(\boldsymbol{Q}_n)\, \boldsymbol{\lambda}_n\right]\,, \\ \boldsymbol{0} &= \boldsymbol{g}(\boldsymbol{Q}_{n+1})\,. \end{aligned}$$

Step 3.

$$\begin{aligned} \boldsymbol{q}_{n+1} &= \boldsymbol{\phi}(\boldsymbol{Q}_{n+1})\,, \\ \boldsymbol{F}_{n+1} &= -[\boldsymbol{\partial_Q \phi}(\boldsymbol{Q}_{n+1})]^T\, \boldsymbol{\nabla_q} U(\boldsymbol{q}_{n+1})\,. \end{aligned}$$

Step 4.

$$\begin{aligned} \boldsymbol{P}_{n+1} &= \boldsymbol{P}_{n+1/2} + \frac{\Delta t}{2}\left[\boldsymbol{F}_{n+1} - \boldsymbol{\nabla_Q g}(\boldsymbol{Q}_{n+1})\, \boldsymbol{\mu}_n\right]\,, \\ \boldsymbol{0} &= \boldsymbol{\partial_Q g}(\boldsymbol{Q}_{n+1})\, \boldsymbol{M}^{-1}\, \boldsymbol{P}_{n+1}\,. \end{aligned}$$

Note that the method is symplectic and, hence, will conserve the total energy $\widehat{H}$ over exponentially long periods of time [3],[14]. Again we like to point out that the modified force field requires additional force field evaluations. However, these additional force field evaluations can be restricted to nearest neighborhood

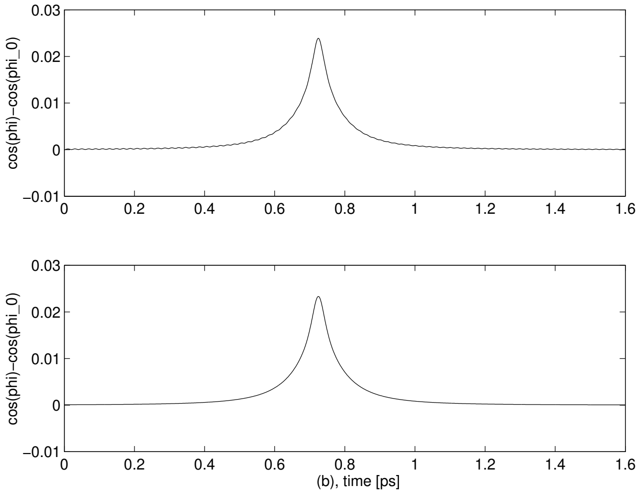

Figure 1: Time evolution of $\cos\phi - \cos\phi_0$ for free dynamics (a) and dynamics with modified force field/soft constraints (b).

interactions. Let us assume that $U_l = U_l^1 + U_l^2$ is such a splitting. Then eq. (10) is replaced by

$$\mathbf{0} \;=\; \boldsymbol{\partial}_{\boldsymbol{Q}}\boldsymbol{g}(\boldsymbol{Q})\boldsymbol{M}^{-1}\left[\boldsymbol{\nabla}_{\boldsymbol{q}}U_l^1(\boldsymbol{q}) + \boldsymbol{\nabla}_{\boldsymbol{q}}U_b(\boldsymbol{q})\right]$$

and the corresponding force field is given by

$$\boldsymbol{F}(\boldsymbol{Q}) \;=\; -[\boldsymbol{\partial}_{\boldsymbol{Q}}\boldsymbol{\phi}(\boldsymbol{Q})]^T\left[\boldsymbol{\nabla}_{\boldsymbol{q}}U_l^1(\boldsymbol{q}) + \boldsymbol{\nabla}_{\boldsymbol{q}}U_b(\boldsymbol{q})\right] - \boldsymbol{\nabla}_{\boldsymbol{Q}}U_l^2(\boldsymbol{Q})\,.$$

The resulting method becomes effective as soon as the number of Newton iterations per time-step is comparable to the number of small time-steps needed in a multiple-time-stepping approach. Note that no resonance induced instabilities can occur.

3 Numerical Experiment

We simulated the collision of two water molecules. The force field was taken from the CHARMM package [6]. Initial conditions were chosen such that no internal vibrations were excited. Fig. 1 gives a comparison of the free dynamics and $\boldsymbol{q} := \boldsymbol{\phi}(\boldsymbol{Q})$ in the bond-angle of one of the water molecules. Note the excellent agreement (standard constrained dynamics would yield $\cos\phi - \cos\phi_0 = 0$). In Fig. 2, we demonstrate the importance of the correct modification of the force field. As shown in (b), the simplified force field

$$\boldsymbol{F}_n \quad = \quad -\boldsymbol{\nabla}_{\boldsymbol{q}}U(\boldsymbol{q}_n)$$

leads to a (small) drift in energy after one collision.

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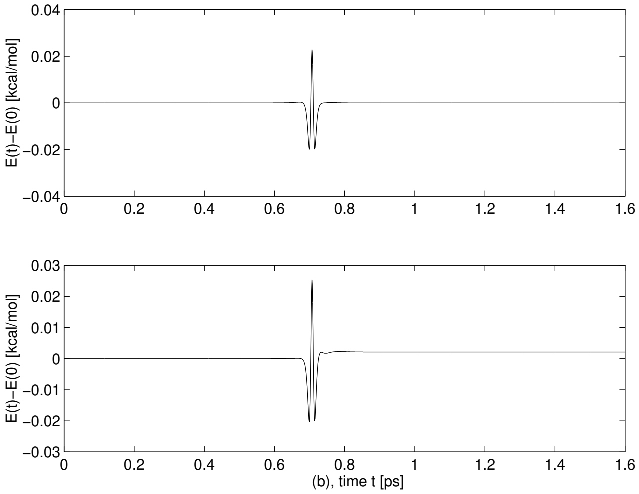

Figure 2: Time evolution of the total energy for "correct" modified force field (a) and "simplified" modified force field (b).

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