

Molecular Dynamics Integration Meets Standard Theory of Molecular Vibrations

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An iterative SISM (split integration symplectic method) for molecular dynamics (MD) integration is described. This work explores an alternative for the internal coordinate system prediction in the SISM introduced by Janežič et al. (*J. Chem. Phys.* 2005, 122, 174101). The SISM, which employs a standard theory of molecular vibrations, analytically resolves the internal high-frequency molecular vibrations. This is accomplished by introducing a translating and rotating internal coordinate system of a molecule and calculating normal modes of an isolated molecule only. The Eckart frame, which is usually used in the standard theory of molecular vibrations as an internal coordinate system of a molecule, is adopted to be used within the framework of the second order generalized leapfrog scheme. In the presented MD integrator the internal coordinate frame at the end of the integration step is predicted halfway through the integration step using a predictor-corrector type iterative approach thus ensuring the method's time reversibility. The iterative SISM, which is applicable to any system of molecules with one equilibrium configuration, was applied here to perform all-atom MD simulations of liquid CO₂ and SO₂. The simulation results indicate that for the same level of accuracy, this algorithm allows significantly longer integration time steps than the standard second-order leapfrog Verlet (LFV) method.

INTRODUCTION

The standard theory of molecular vibrations was originally developed to study the rotation–vibration spectra of molecular gases.¹ In this theory it is assumed that the Born–Oppenheimer approximation in separating the electron and nuclear degrees of freedom is valid and the dynamical molecular model² is used to describe the structure and dynamics of a molecule. A molecule is supposed to consist of point-masses (atoms) that are held together by forces stemming from the potential defined by the motions of electrons. The forces between neighboring atoms in a molecule can be represented by weightless harmonic springs that obey Hooke's law, so that a molecule can be thought of as a system of coupled harmonic oscillators obeying the classical equations of motion. The interactions between separate molecules are neglected.¹ A molecule can translate and rotate around its center-of-mass, while at the same time the atoms can vibrate around their equilibrium positions defined by the minima of the potential. While translation of a molecule is uncoupled from the vibrational and rotational degrees of freedom and can be treated separately, this is not the case for coupled rotation and vibration of a molecule. To handle the rotation–vibration problem, the internal coordinate system of a molecule that rotates with the molecule is introduced.¹ A set of conditions that define the internal coordinate system—the Eckart frame, which allows for an optimum separation of rotation and vibration was introduced in ref 3 for the case of nonlinear molecules with one equilibrium configuration and no internal rotation. It was assumed that the displacements of the atoms from their equilibrium positions defined by the moving Eckart frame are sufficiently small. The extension to linear molecules was

presented in ref 4. The special importance of the Eckart frame is that it enables the introduction of the normal coordinates in the terms of which the coupled vibrations of a molecule become uncoupled and thus analytically treatable.⁵

A similar physical picture as in the standard theory of molecular vibrations is also used in all-atom molecular dynamics (MD) simulations.^{6–8} In all-atom MD simulations atoms are also treated as classical point-mass particles, and the classical equations of motion are integrated for all atoms in the system to simulate the behavior of the molecular system. Here, as opposed to the standard theory of molecular vibrations, the amplitudes of vibration may not be small but can vary by large amounts. The interactions, e.g., the electrostatic and van der Waals interactions, between different molecules are also taken into account, so that more complex molecular systems, e.g., liquids, can also be treated. The equations describing the motion of these systems usually do not have an analytical solution, and therefore the solution can only be obtained by numerical integration.^{6,9}

New semianalytical second order symplectic integrators, developed by combining the molecular dynamics (MD) integration and the standard theory of molecular vibrations, were presented in refs 10–12. The unique feature of these MD integrators is in that the standard theory of molecular vibrations, which is a very efficient tool to analyze the dynamics of the studied system from computed trajectories,^{13–19} is used not to analyze but to compute trajectories of molecular systems. Information about the energy distribution of normal modes and the energy transfer between them is obtained without additional calculations.²⁰ The analytical description of coupled molecular vibrations, which is employed by the methods presented in refs 10–12, is possible only by using the normal coordinates¹ and a translating and rotating internal coordinate system of each

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molecule.^{2,3} The dynamics of an Eckart frame had to be adopted to be used within the second-order generalized leapfrog scheme^{21,22} for MD integration. To ensure the time-reversibility of the methods the internal coordinate system was predicted at the beginning of an integration step to yield the exact equilibrium configuration of a molecule halfway through the integration step.

In the present work we explore an alternative for the internal coordinate system prediction, which is here made not at the beginning but halfway through the integration step. As opposed to the method presented in the previous work in ref 10, here, an iterative procedure as in the predictor-corrector type numerical methods is employed to predict the internal coordinate system for the end of the integration step giving rise to iterative version of Split Integration Symplectic Method (SISM). The method presented here was applied to perform all-atom MD simulations of liquid CO₂ and SO₂. The numerical results indicate that the iterative SISM, due to the analytical treatment of high-frequency motions, allows considerably longer integration time steps than the standard LFV algorithm²³ for the same computational accuracy and computational cost per integration step.

2. INTERNAL COORDINATE SYSTEM

First, we define a fixed Cartesian coordinate system and denote the instantaneous position vectors of N atoms of a molecule relative to its origin by $\mathbf{r}_\alpha \in \mathbf{R}^3$, $\alpha = 1, 2, \dots, N$.¹⁰ Next, we introduce the translating and rotating internal coordinate system of the molecule, which is attached to the molecule and moves with it. Usually the Eckart frame^{2,3} is chosen to be the internal coordinate system, which is the internal coordinate system where the coupling between the vibrational and rotational degrees of freedom of a molecule is zero at equilibrium. The Eckart frame is defined by the right-handed triad of unit vectors \mathbf{f}_i , $i = 1, 2, 3$, where $\mathbf{f}_i \cdot \mathbf{f}_k = \delta_{jk}$, with the origin in the center-of-mass of a molecule. The unit vectors are uniquely defined by the instantaneous positions \mathbf{r}_α of atoms in the molecule, by the masses of atoms m_α , and by the constant equilibrium distances of the atoms from the molecule's center-of-mass c_i^α , $i = 1, 2, 3$ satisfying $\sum_\alpha m_\alpha c_i^\alpha = 0$.² The internal coordinate system can be attached to the equilibrium configuration of a molecule in different ways, each of which yields a different Eckart frame. Nevertheless, once we have made a definite choice, the Eckart frame is defined in a unique way.

The equilibrium positions of atoms relative to the molecule's center-of-mass are given by vectors \mathbf{c}_α

$$\mathbf{c}_\alpha = \sum_i c_i^\alpha \mathbf{f}_i \quad (1)$$

The equilibrium positions of atoms in the Cartesian coordinate system are given by

$$\mathbf{d}_\alpha = \mathbf{R} + \mathbf{c}_\alpha \quad (2)$$

where \mathbf{R} is the center-of-mass vector

$$\mathbf{R} = \sum_\alpha m_\alpha \mathbf{r}_\alpha / \sum_\alpha m_\alpha \quad (3)$$

The displacement vectors of atoms from their equilibrium position are therefore defined as

$$\boldsymbol{\rho}_\alpha = \mathbf{r}_\alpha - \mathbf{d}_\alpha \quad (4)$$

If the displacement vectors are written in terms of the internal coordinate system, the relative Cartesian displacement coordinates are

$$\boldsymbol{\rho}_\alpha = (\boldsymbol{\rho}_\alpha \cdot \mathbf{f}_1) \mathbf{f}_1 + (\boldsymbol{\rho}_\alpha \cdot \mathbf{f}_2) \mathbf{f}_2 + (\boldsymbol{\rho}_\alpha \cdot \mathbf{f}_3) \mathbf{f}_3 = \Delta x_\alpha \mathbf{f}_1 + \Delta y_\alpha \mathbf{f}_2 + \Delta z_\alpha \mathbf{f}_3 \quad (5)$$

where \mathbf{f}_1 points along the x direction, \mathbf{f}_2 along the y direction, and \mathbf{f}_3 along the z direction of the internal coordinate system.

The unit vectors \mathbf{f}_1 , \mathbf{f}_2 , and \mathbf{f}_3 are determined from three Eckart vectors \mathcal{F}_1 , \mathcal{F}_2 , and \mathcal{F}_3 , which are introduced as in ref 2

$$\mathcal{F}_i = \sum_\alpha m_\alpha c_i^\alpha \mathbf{r}_\alpha \quad (6)$$

where m_α is the mass of the α atom in the molecule. In the example of nonlinear and nonplanar molecules $\mathbf{f} = (\mathbf{f}_1, \mathbf{f}_2, \mathbf{f}_3)$ are computed as

$$\mathbf{f} = \mathcal{F} \cdot \mathcal{G}^{-1/2} \quad (7)$$

where $\mathcal{F} = (\mathcal{F}_1, \mathcal{F}_2, \mathcal{F}_3)$ and \mathcal{G} is a symmetric positive definite Gram matrix defined as

$$\mathcal{G} = \mathcal{F} \otimes \mathcal{F} \quad (8)$$

Here \otimes denotes the tensor product of two vectors. The matrix $\mathcal{G}^{-1/2}$ is a positive definite matrix for which $\mathcal{G}^{-1/2} \cdot \mathcal{G}^{-1/2} = \mathcal{G}^{-1}$ holds, where \mathcal{G}^{-1} is the positive definite inverse of \mathcal{G} .²

The vectors \mathbf{f}_i , $i = 1, 2, 3$ satisfy the Eckart conditions for the orientation of the Eckart frame^{2,3}

$$\sum_\alpha m_\alpha \mathbf{c}_\alpha \times \boldsymbol{\rho}_\alpha = 0 \quad (9)$$

which state that there is no angular momentum with respect to the internal coordinate system in the zeroth order of displacements of the atoms from their equilibrium positions.¹

In the case of planar molecules, $c_3^\alpha = 0$ holds. Therefore,²

$$(\mathbf{f}_1, \mathbf{f}_2) = (\mathcal{F}_1, \mathcal{F}_2) \cdot \mathcal{G}^{-1/2} \quad (10)$$

$$\mathbf{f}_3 = \mathbf{f}_1 \times \mathbf{f}_2 \quad (11)$$

where \times denotes the vector product of two vectors, and \mathcal{G} is a symmetric 2×2 matrix defined by

$$\mathcal{G} = (\mathcal{F}_1, \mathcal{F}_2) \otimes (\mathcal{F}_1, \mathcal{F}_2) \quad (12)$$

In the example of linear molecules, only one unit vector, \mathbf{f}_3 , can be uniquely defined. The other two, \mathbf{f}_1 and \mathbf{f}_2 , are arbitrary unit vectors determined in such a way that the mutual orthogonality between all of them holds.^{4,24} Unit vector \mathbf{f}_3 points along the axis of the molecule and is determined from the condition (9)

$$\mathbf{f}_3 = \sum_\alpha m_\alpha c_i^\alpha \mathbf{r}_\alpha / |\sum_\alpha m_\alpha c_i^\alpha \mathbf{r}_\alpha| \quad (13)$$

where $|\cdot|$ denotes the norm of the vector. Without loss of

generality, the second component of \mathbf{f}_{2y} can be set to 0. The first and the third one (\mathbf{f}_{2x} and \mathbf{f}_{2z} , respectively) are determined from

$$\mathbf{f}_1 \cdot \mathbf{f}_2 = 0 \quad (14)$$

$$|\mathbf{f}_2| = 1 \quad (15)$$

where \mathbf{f}_1 is orthogonal to both \mathbf{f}_2 and \mathbf{f}_3 :

$$\mathbf{f}_1 = \mathbf{f}_2 \times \mathbf{f}_3 \quad (16)$$

3. DESCRIPTION OF MOLECULAR DEGREES OF FREEDOM IN TERMS OF NORMAL COORDINATES

Using the internal coordinate system we can define equilibrium positions of the atoms in a molecule in such a way that the displacements of the atoms Δq_i are sufficiently small, so that the normal-mode analysis can be applied.

In normal-mode analysis only quadratic terms are kept in the expansion of the vibrational potential energy V_{vib} and all higher terms are neglected¹

$$\begin{aligned} V_{\text{vib}} \approx V_{\text{harm}} &= \frac{1}{2} \sum_{i,j=1}^{3N} \left(\frac{\partial^2 V_{\text{vib}}}{\partial \Delta q_i \partial \Delta q_j} \right)_0 \Delta q_i \Delta q_j = \\ &= \frac{1}{2} \sum_{i,j=1}^{3N} \left(\frac{\partial^2 V_{\text{harm}}}{\partial \Delta q_i \partial \Delta q_j} \right)_0 \Delta q_i \Delta q_j \\ &= \frac{1}{2} \sum_{i,j=1}^{3N} H_{ij} \Delta q_i \Delta q_j = \frac{1}{2} \Delta \mathbf{q} \cdot \mathbf{H} \cdot \Delta \mathbf{q} \end{aligned} \quad (17)$$

Here $\Delta \mathbf{q} = (\Delta x_1, \Delta y_1, \Delta z_1, \dots, \Delta x_N, \Delta y_N, \Delta z_N)$ is a vector of the relative Cartesian displacement coordinates and their corresponding momenta are $\Delta \mathbf{p} = (m_1 \Delta v_{1x}, m_1 \Delta v_{1y}, m_1 \Delta v_{1z}, \dots, m_N \Delta v_{Nx}, m_N \Delta v_{Ny}, m_N \Delta v_{Nz})$, where subscripts x, y, z denote x, y, z components of the internal coordinate system, respectively. The Hessian $\mathbf{H} \in \mathbf{R}^{3N \times 3N}$ is a symmetric matrix of the second derivatives of the vibrational potential energy with the elements

$$H_{ij} = H_{ji} = \left(\frac{\partial^2 V_{\text{vib}}}{\partial \Delta q_i \partial \Delta q_j} \right)_0 = \left(\frac{\partial^2 V_{\text{harm}}}{\partial \Delta q_i \partial \Delta q_j} \right)_0 \quad (18)$$

To determine the vibrational motions of the system, the eigenvalues and eigenvectors of the mass-weighted Hessian $\mathbf{M}^{-1/2} \cdot \mathbf{H} \cdot \mathbf{M}^{-1/2}$ have to be calculated.^{1,16-18} This leads to solving a secular equation

$$\det(\mathbf{M}^{-1/2} \cdot \mathbf{H} \cdot \mathbf{M}^{-1/2} - \lambda \mathbf{I}) = 0 \quad (19)$$

where $\mathbf{M} \in \mathbf{R}^{3N \times 3N}$ is a diagonal mass matrix. The diagonal elements are $M_{11} = m_1, M_{22} = m_1, M_{33} = m_1, \dots, M_{3N-2, 3N-2} = m_N, M_{3N-1, 3N-1} = m_N, M_{3N, 3N} = m_N$. For a nonlinear molecule composed of N atoms, eq 19 has $3N - 6$ nonzero eigenvalues $\omega_i = \sqrt{\lambda_i}$ describing molecular vibrations. The corresponding dynamics is described in the standard theory of molecular vibration by normal coordinates $Q_i, i = 1, 2, \dots, 3N - 6$.²⁵ Six of $3N$ roots in eq 19 are zero. They correspond to three translations and three rotations of a molecule as a whole, while their dynamics is not described in terms of the normal coordinates.^{1,10}

An alternative approach to the standard theory's description of a molecule's rotation and translation¹ is to describe rotation and translation of a molecule in terms of the normal coordinates. To do so the whole atom velocity needs to be expressed in terms of the relative Cartesian displacement coordinates. This approach was presented in full detail in ref 10 where it was shown that the dynamics of the internal coordinate system in this case differs from the dynamics of the Eckart frame, which is employed in the standard theory of molecular vibrations.

The equations of motion for the normal coordinates take the Hamiltonian form¹⁰

$$\frac{d}{dt} P_i = -\omega_i^2 Q_i; \quad \frac{d}{dt} Q_i = P_i, \quad i = 1, 2, \dots, 3N \quad (20)$$

where P_i is the conjugate momentum to the normal coordinate Q_i .²⁵

The particular solution of the system (20) can be written as¹⁰

$$\begin{bmatrix} P_i(\frac{\Delta t}{2}) \\ Q_i(\frac{\Delta t}{2}) \end{bmatrix} = \begin{bmatrix} \cos(\omega_i \frac{\Delta t}{2}) & -\omega_i \sin(\omega_i \frac{\Delta t}{2}) \\ \frac{1}{\omega_i} \sin(\omega_i \frac{\Delta t}{2}) & \cos(\omega_i \frac{\Delta t}{2}) \end{bmatrix} \begin{bmatrix} P_i(0) \\ Q_i(0) \end{bmatrix} \quad (21)$$

Eq 21 describes vibrational motion corresponding to the normal mode i with $\omega_i > 0$.

The equations of motion for the translation and rotation of a molecule in terms of the normal coordinates, obtained from eq 21 for the normal coordinates with $\omega_i = 0$ and using $\lim_{x \rightarrow 0} \sin x/x = 1$, are¹⁰

$$P_i(\frac{\Delta t}{2}) = P_i(0) \quad (22)$$

$$Q_i(\frac{\Delta t}{2}) = P_i(0) \frac{\Delta t}{2} + Q_i(0) \quad (23)$$

The expressions for the transformations between Cartesian, relative Cartesian displacement, and normal coordinates are obtained in a straightforward way and are presented in ref 10.

4. ITERATIVE SISIM

In the MD simulation the Hamilton equations are solved for each atom of the system

$$\frac{d\boldsymbol{\eta}}{dt} = \{\boldsymbol{\eta}, H\} = \hat{L}_H \boldsymbol{\eta} \quad (24)$$

where \hat{L}_H is the Lie operator, $\{\cdot, \cdot\}$ is the Poisson bracket,²⁵ and $\boldsymbol{\eta} = (\mathbf{q}, \mathbf{p})$ is a vector of the coordinates of all the particles and their conjugate momenta.

The formal solution of the Hamiltonian system (24) can be written in terms of Lie operators as

$$\boldsymbol{\eta}|_{t_k+\Delta t} = \exp(\Delta t \hat{L}_H) \boldsymbol{\eta}|_{t_k} \quad (25)$$

and represents the exact time evolution of a trajectory in phase space composed of coordinates and momenta of all the particles from t_k to $t_k + \Delta t$, where Δt is the integration time step.²⁵

First, we split the Hamiltonian H of a system into two parts¹⁰

$$H = H_0 + H_r \quad (26)$$

where H_0 is the part of the Hamiltonian that can be solved analytically and H_r is the remaining part.

Next, a second-order approximation for (25), known as the generalized leapfrog scheme,^{21,22} is used

$$\boldsymbol{\eta}|_{t_{k+1}} = \exp\left(\frac{\Delta t}{2}\hat{L}_{H_0}\right)\exp(\Delta t\hat{L}_{H_r})\exp\left(\frac{\Delta t}{2}\hat{L}_{H_0}\right)\boldsymbol{\eta}|_{t_k} + \mathcal{O}(\Delta t^3) \quad (27)$$

which defines the Split Integration Symplectic Method (SISM).¹⁰ The whole integration time step combines the analytical evolution of H_0 with a correction arising from the H_r resolved by numerical integration.

The model Hamiltonian has the following form

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2} \sum_{\text{bonds}} k_b (b - b_0)^2 + \frac{1}{2} \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 + \sum_{i>j} \frac{e_i e_j}{4\pi\epsilon_0 r_{ij}} + \sum_{i>j} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (28)$$

where i and j run over all atoms, m_i is the mass of the i th atom, \mathbf{p}_i is the linear momentum of the i th atom, b_0 and θ_0 are reference values for bond lengths and angles, respectively, k_b and k_θ are corresponding force constants, e_i denotes the charge on the i th atom, ϵ_0 is the dielectric constant in a vacuum, r_{ij} is the distance between the i th and j th atoms, and ϵ_{ij} and σ_{ij} are the corresponding constants of the Lennard-Jones potential.

The total vibrational potential energy of the system is the sum of vibrational potential energies of all the molecules in the system¹⁰

$$V_{\text{vib}} = \sum_{j=1}^m V_{\text{vib}_j} = \frac{1}{2} \sum_{\text{bonds}} k_b (b - b_0)^2 + \frac{1}{2} \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 \quad (29)$$

where V_{vib_j} is the vibrational potential energy of the j th molecule.

The pure harmonic H_0 in the splitting (26) is defined as the sum of vibrational energies of all the molecules in the system¹⁰

$$H_0 = T + V_{\text{harm}} = \sum_{j=1}^m (T_j + V_{\text{harm}_j}) \quad (30)$$

where $T = \sum_i \mathbf{p}_i^2/2m_i$ is the kinetic energy of all the atoms in the systems, T_j is the kinetic energy of the j th molecule, V_{harm} is the harmonic vibrational potential energy, which is for an individual molecule defined by eq 17, V_{harm_j} is the corresponding harmonic vibrational potential energy of the j th molecule, and m is the number of all the molecules in the system.

The remaining part of the Hamiltonian

$$H_r = H - H_0 = V_{\text{nb}} + V_{\text{ah}} \quad (31)$$

is then equal to the sum of the nonbonded potential energy

$$V_{\text{nb}} = \sum_{i>j} \frac{e_i e_j}{4\pi\epsilon_0 r_{ij}} + \sum_{i>j} 4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (32)$$

and the anharmonic vibrational potential energy of higher terms (cubic, quartic, etc.) in terms of displacements of atoms from their equilibrium positions is

$$V_{\text{ah}} = V_{\text{vib}} - V_{\text{harm}} = \frac{1}{2} \sum_{\text{bonds}} k_b (b - b_0)^2 + \frac{1}{2} \sum_{\text{angles}} k_\theta (\theta - \theta_0)^2 - V_{\text{harm}} \quad (33)$$

Each molecule is treated as an isolated molecule when propagated by $\exp(\Delta t/2\hat{L}_{H_0})$. Propagation by $\exp(\Delta t/2\hat{L}_{H_0})$ is solved analytically permitting a longer integration time step to be used by the SISM.

As demonstrated in ref 10 the equations of motion that describe the dynamics of the internal coordinate system used by our approach are different from the corresponding equations of motion for the Eckart frame. In ref 10 we derived the equations of motion for the internal coordinate system from the method's time-reversibility condition. It was shown that the internal coordinate system is fixed over the evolution with $\exp(\Delta t/2\hat{L}_{H_0})$. Therefore it can be only moved either at the beginning or in the middle (evolution with $\exp(\Delta t\hat{L}_{H_r})$) of the integration step. In ref 10 we only explored the possibility that the internal coordinate system is moved at the beginning of an integration step to yield the exact equilibrium configuration of a molecule halfway through the integration step.

Here we present an alternative approach, in which we change the internal coordinate system halfway through the integration step to yield the exact equilibrium configuration of a molecule at the end of the integration step. The algorithm for the iterative SISM obtained in this way is, for each molecule in the system, the following:

0. Initialization. At the outset of a simulation the vibrational frequencies and normal mode vectors of the mass-weighted Hessian $\mathbf{M}^{-1/2} \cdot \mathbf{H} \cdot \mathbf{M}^{-1/2}$, where \mathbf{H} is defined by eq 18 for an isolated molecule only, are computed. Also the transformational matrix \mathbf{A} between the relative Cartesian displacement and normal coordinates is determined. The columns of \mathbf{A} are the eigenvectors of $\mathbf{M}^{-1/2} \cdot \mathbf{H} \cdot \mathbf{M}^{-1/2}$.

Using the initial position of atoms at the outset of a simulation $\mathbf{w}_0 = \mathbf{q}(t=0)$, the internal coordinate system of a molecule is determined using eqs 3, 6, 7, and 8. Next, the Cartesian coordinates $\mathbf{q}(0)$, $\mathbf{p}(0)$ are transformed to relative Cartesian displacement coordinates $\Delta\mathbf{q}(0)$, $\Delta\mathbf{p}(0)$ ¹⁰ and the relative Cartesian displacement coordinates $\Delta\mathbf{q}(0)$, $\Delta\mathbf{p}(0)$ are transformed to the normal coordinates $Q_i(0)$, $P_i(0)$:

$$Q_i(0) = \sum_{l=1}^{3N} \sqrt{M_{ll}} A_{li} \Delta q_l(0) \quad (34)$$

$$P_i(0) = \sum_{l=1}^{3N} \frac{1}{\sqrt{M_{ll}}} A_{li} \Delta p_l(0) \quad (35)$$

The obtained $Q_i(0)$ and $P_i(0)$ are then used as the initial values of Q_{i_1} and P_{i_1} in the first integration step of a simulation: $Q_{i_1} = Q_i(0)$ and $P_{i_1} = P_i(0)$ where Q_{i_k} and P_{i_k} are the normal coordinates at the beginning of the k th integration step. Step 0 is performed only once at the outset of a simulation.

1. Propagation by $\exp((\Delta t/2)\hat{L}_{H_0})$. Rotation of $Q_{i_k}, P_{i_k}, i = 1, \dots, 3N$ in phase space by corresponding vibrational frequency ω_i for $\Delta t/2$ to obtain $Q'_{i_k}, P'_{i_k}, i = 1, \dots, 3N$ using eq 21 for vibration ($\omega_i \neq 0$) and eqs 22 and 23 for translation and rotation ($\omega_i = 0$).

2. Transformation of the normal coordinates $Q'_{i_k}, P'_{i_k}, i = 1, \dots, 3N$ to the relative Cartesian displacement coordinates $\Delta \mathbf{q}'_k, \Delta \mathbf{p}'_k$.¹⁰

3. Transformation of the relative Cartesian displacement coordinates $\Delta \mathbf{q}'_k, \Delta \mathbf{p}'_k$ to the Cartesian coordinates $\mathbf{q}'_k, \mathbf{p}'_k$.¹⁰

4. Evolution by $\exp(\Delta t \hat{L}_{H_r})$. The numerical integration of momenta (force calculation):

4a. The harmonic force $\mathbf{F}_k(\Delta \mathbf{q}'_k)$ is calculated where it is taken into account that $\mathbf{f}_1, \mathbf{f}_2,$ and \mathbf{f}_3 are fixed and no system forces are present. The momenta are changed next

$$\mathbf{p}''_k = \mathbf{p}'_k + \frac{\Delta t}{2} \left(\frac{-\partial V_{\text{vib}}}{\partial \mathbf{q}}(\mathbf{q}'_k) - \mathbf{F}_k \right) \quad (36)$$

$$\mathbf{p}'''_k = \mathbf{p}''_k - \Delta t \frac{\partial V_{\text{nb}}}{\partial \mathbf{q}(\mathbf{q}'_k)} \quad (37)$$

where $\partial/\partial \mathbf{q} = (\partial/\partial q_1, \partial/\partial q_2, \dots, \partial/\partial q_{3N})$. The vector \mathbf{F} is defined as $\mathbf{F} = (\mathbf{F}_1, \mathbf{F}_2, \dots, \mathbf{F}_N)$, where

$$\mathbf{F}_\alpha = -\frac{\partial V_{\text{harm}}}{\partial \Delta x_\alpha} \mathbf{f}_1 - \frac{\partial V_{\text{harm}}}{\partial \Delta y_\alpha} \mathbf{f}_2 - \frac{\partial V_{\text{harm}}}{\partial \Delta z_\alpha} \mathbf{f}_3$$

is the harmonic intramolecular force acting on atom α .

4b. Prediction of Moving and Rotating Internal Coordinate System. The internal coordinate system of a molecule is in the zeroth iteration redefined using eqs 3, 6, 7, and 8 and the positions \mathbf{w}_k defined as

$$\mathbf{w}_k = \mathbf{q}'_k + \mathbf{M}^{-1} \cdot \mathbf{p}'''_k \frac{\Delta t}{2} \quad (38)$$

For all the following iterations the internal coordinate system is the one defined in step 9.

4c. Back transformation from the Cartesian coordinates \mathbf{q}'_k to the relative Cartesian displacement coordinates $\Delta \mathbf{q}''_k$ ¹⁰ using the new internal coordinate system.

4d. The new harmonic force $\mathbf{F}'_k(\Delta \mathbf{q}''_k)$ is calculated and momenta are changed accordingly:

$$\mathbf{p}''''_k = \mathbf{p}'''_k + \frac{\Delta t}{2} \left(\frac{-\partial V_{\text{vib}}}{\partial \mathbf{q}}(\mathbf{q}'_k) - \mathbf{F}'_k \right) \quad (39)$$

V_{harm} is redefined with respect to the new internal coordinate system. V_{vib} remains unchanged with the redefinition of the internal coordinate system. Therefore the previously calculated forces $-\partial V_{\text{vib}}/\partial \mathbf{q}(\mathbf{q}'_k)$ are used.

Since $H_r = H_r(\mathbf{q})$, $[(\partial H_r/\partial \mathbf{p}) = 0]$, only momenta are changed in step 4:

$$\mathbf{q}'_k = \mathbf{q}'_k + \Delta t \partial H_r / \partial \mathbf{p}(\mathbf{p}'_k) = \mathbf{q}'_k \quad (40)$$

5. Back transformation from the Cartesian coordinates \mathbf{p}''''_k , to the relative Cartesian displacement coordinates $\Delta \mathbf{p}''_k$.¹⁰

6. Back transformation from the relative Cartesian displacement coordinates $\Delta \mathbf{q}''_k, \Delta \mathbf{p}''_k$ to the normal coordinates $Q''_{i_k}, P''_{i_k}, i = 1, \dots, 3N$.¹⁰

7. Propagation by $\exp((\Delta t/2)\hat{L}_{H_0})$. Again, rotation of the normal coordinates in phase space for $\Delta t/2$ to obtain $Q_{i_{k+1}}, P_{i_{k+1}}, i = 1, \dots, 3N$ using eq 21 for vibration ($\omega_i \neq 0$) and eqs 22 and 23 for translation and rotation ($\omega_i = 0$).

8. Back transformation from the normal coordinates $Q_{i_{k+1}}, P_{i_{k+1}}, i = 1, \dots, 3N$ to the relative Cartesian displacement coordinates $\Delta \mathbf{q}_{k+1}, \Delta \mathbf{p}_{k+1}$ and to the Cartesian coordinates $\mathbf{q}_{k+1}, \mathbf{p}_{k+1}$.¹⁰

9. Comparison of predicted (step 4b) and new (actual) internal coordinate systems calculated from \mathbf{q}_{k+1} using eqs 3, 6, 7, and 8. If the agreement between the predicted and actual internal coordinate systems is inadequate, then return to step 4b and use the new internal coordinate system otherwise go to 1.

This algorithm holds for every atom in a molecule and for every molecule in the system. Only the potential V_{nb} in eq 32 is the function that depends on all the coordinates of all the atoms in the system not only on the coordinates of atoms in a single molecule.

To move the internal coordinate system halfway through the integration step, the algorithm needs to be symmetric relative to the point where the internal coordinate system is moved. In the propagation $\exp(\Delta t \hat{L}_{H_r})$ the long-range and the anharmonic forces are computed, and according to them, the momenta changed at the constant position of the atoms. The long-range forces and the bond stretching and angle bending forces computed from the whole bond stretching and angle bending potential, V_{vib} , are independent of the definition of the internal coordinate system. This is not the case for the harmonic forces computed from the true harmonic potential V_{harm} in terms of the relative displacement Cartesian coordinates. Therefore the part of the algorithm where the correction due to anharmonic potential V_{ah} is computed has to be split into two parts. In each of them the same V_{vib} potential is used, whereas in the first part, V_{harm} is determined in terms of the old internal coordinate system (step 4a) while in the second one in terms of the new one (step 4d). The drawback of this approach is that the harmonic forces need to be calculated twice per each integration step. However, since they are short-ranged, their computational complexity is linear, and the computational complexity for computation of long-range forces prevails.

The configuration \mathbf{w}_k from which the new internal coordinate system is obtained using eqs 6–8 is derived as follows. The linear momentum $\mathbf{p} = (p_1, p_2, \dots, p_{3N}) = (\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N)$ of a given molecule with N atoms can be split into a vibrational, rotational, and translational contribution as

$$\mathbf{p} = \mathbf{p}^{\text{vib}} + \mathbf{p}^{\text{rot}} + \mathbf{p}^{\text{trans}} \quad (41)$$

where \mathbf{p}^{vib} is the vibrational part, \mathbf{p}^{rot} is the rotational part, and $\mathbf{p}^{\text{trans}}$ is the translational part of the linear momentum, respectively. From the dynamics governed by the normal modes corresponding to vibrational frequency zero ($\omega = 0$) as described by eqs 22 and 23 it follows that $\mathbf{p}^{\text{rot}} + \mathbf{p}^{\text{trans}}$ is

a constant of motion during the propagation by $\exp((\Delta t/2)\hat{L}_{H_0})$. Only this part of the linear momentum changes the equilibrium configuration of a molecule (the rotational part changes the orientation, the translational part moves the origin of the internal coordinate system), whereas the vibrational part of the linear momentum determines only the displacements of atoms from their equilibrium positions.

Using eqs 38 and 41 we can rewrite \mathbf{w}_k as

$$\mathbf{w}_k = \mathbf{q}'_k + \mathbf{M}^{-1} \cdot \mathbf{p}'''_k \frac{\Delta t}{2} = \mathbf{q}'_k + \mathbf{M}^{-1} \cdot (\mathbf{p}'''_k{}^{\text{vib}} + \mathbf{p}'''_k{}^{\text{rot}} + \mathbf{p}'''_k{}^{\text{trans}}) \frac{\Delta t}{2} \quad (42)$$

The coordinates \mathbf{w}_k defined by eq 38 would therefore define the same internal coordinate system of a molecule as the actual atoms' coordinates at the end of the integration step if the torque arising from potential V_{harm} in the second part of the propagation by $\exp(\Delta t \hat{L}_{H_t})$ (step 4d) did not change $\mathbf{p}'''_k{}^{\text{rot}}$. Although the harmonic forces are internal forces and their sum is zero, they do not lie along bonds joining neighboring atoms. Therefore they do not satisfy the condition of the strong law of action and reaction and their torque changes $\mathbf{p}'''_k{}^{\text{rot}}$.²⁵ Despite this, eq 38 is a good prediction of the conformation of the molecule defining the same Eckart frame as the actual conformation at the end of the integration step. However, it is not accurate to ensure the time reversibility of the algorithm.¹⁰ This obstacle is overcome by the iteration, where eq 38 is used in the middle of the integration step to predict the Eckart frame at the end of the integration step. Then the remaining part of the integration step is performed where at the end the actual Eckart frame is determined from the actual atom positions at the end of the integration step and then compared with the predicted one. If the agreement between these two coordinate systems is inadequate, we return to the middle of the integration step, use the Eckart frame from the end of the integration step from previous iteration, and repeat the remaining part of the integration step. We iterate until the agreement between the predicted and actual Eckart frame is satisfactory. The quality of the internal coordinate system prediction is evaluated by eq 7. From the atom displacements at the end of the integration step we check whether the predicted internal coordinate system corresponds to the Eckart frame (up to the machine accuracy) at the end of the integration step. Because we repeat only the part of the integration step where long-range forces are not computed, the additional computational complexity is linear. Our simulation results indicate that the convergence is usually reached after two iterations. Since the dynamics of the internal coordinate system is time-reversible the presented MD integrator is also time-reversible, a necessary condition for all symmetric symplectic integrators.²⁶

The prediction (38) together with eqs 22 and 23 governs the dynamics of the equilibrium configuration of a molecule, while the atom vibrations around their equilibrium positions are determined by eq 21.

Owing to the introduction of the translating and rotating internal coordinate system of a molecule, the Hessian \mathbf{H} defined by eq 18 is diagonalized only once at the beginning of a simulation, in step 0. This holds only for molecules with one equilibrium configuration and no internal rotation. Since

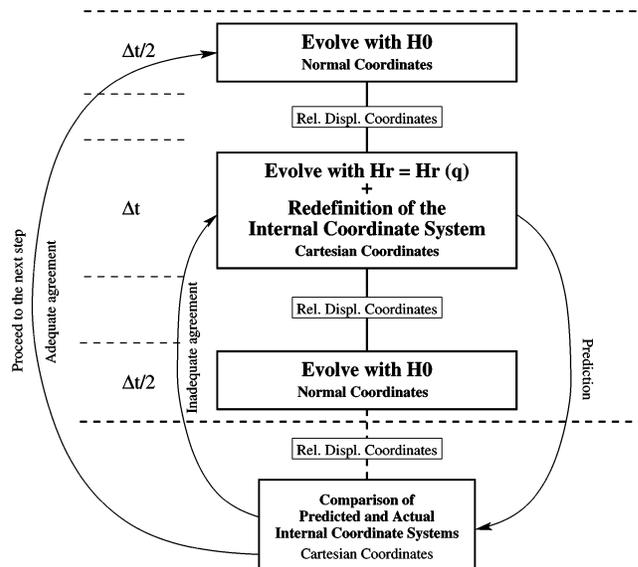


Figure 1. Solution scheme for iterative SISM.

Table 1. Normal Mode Frequencies of the CO₂ Molecule

normal mode	1/λ [cm ⁻¹]: experiment ^a	1/λ [cm ⁻¹]: theory ^b
antisymmetric C–O stretching	2349	2410
symmetric C–O stretching	1333	1258
angle bending	667	667

^a Experimental,²⁸ ^b Theoretical.³⁰

the displacements of atoms from their moving equilibrium positions are always sufficiently small, eq 17 holds at any moment. Therefore the Hessian \mathbf{H} , defined by eq 18, is the same constant matrix for the entire simulation. The iterative SISM is schematically presented in Figure 1.

5. NUMERICAL EXPERIMENTS

The presented iterative SISM was evaluated on a model system of 1024 linear carbon dioxide molecules (CO₂) and planar sulfur dioxide molecules (SO₂).

The model Hamiltonian is in both examples given by eq 28. The derivation of the corresponding Hessians defined by eq 18 is presented elsewhere.^{11,12,27}

Carbon Dioxide (CO₂). The experimental value²⁸ was taken for the reference bond length between carbon and oxygen atoms in the CO₂ molecule. Partial charges and Lennard-Jones potential parameters are taken from ref 29. The bond stretching and angle bending force constants were obtained by fitting the normal-mode frequencies of the CO₂ molecule calculated analytically³⁰ to the corresponding experimental values²⁸ (see Table 1). Our parameters of the Hamiltonian (28) given in Table 2 are in good agreement with the force-field parameters from ref 31.

We have carried out the MD simulation of a system of 1024 CO₂ molecules with the density $\rho = 1.179$ g/cm³ at $T = 216.6$ K corresponding to the liquid state.²⁸ The corresponding size of the simulation box was $a = 39.88$ Å. Periodic boundary conditions were imposed to overcome the problem of surface effects; the minimum image convention was used.⁶ The Coulomb interactions were truncated using

Table 2. Parameters of Hamiltonian (28) for CO₂ Molecule

parameter	value
$b_{O_1C_0} = b_{1_0}$	1.160 Å
$b_{CO_2_0} = b_{2_0}$	1.160 Å
θ_0	0°
$k_{b_{O_1C}} = k_{b_1}$	2150.0 kcal/mol/Å ²
$k_{b_{CO_2}} = k_{b_2}$	2150.0 kcal/mol/Å ²
$k_\theta = k_{\theta_1}$	111.0 kcal/mol/radian ²
$e_{O_1} = e_1$	-0.255 e_0
$e_C = e_2$	0.51 e_0
$e_{O_2} = e_3$	-0.255 e_0
σ_{OO}	3.264 Å
σ_{CC}	3.126 Å
ϵ_{OO}	0.1651 kcal/mol
ϵ_{CC}	0.0576 kcal/mol

Table 3. Normal Mode Frequencies of the SO₂ Molecule

normal mode	1/λ [cm ⁻¹]: experiment ^a	1/λ [cm ⁻¹]: theory ^b
antisymmetric S–O stretching	1362	1398
symmetric S–O stretching	1151	1205
angle bending	518	599

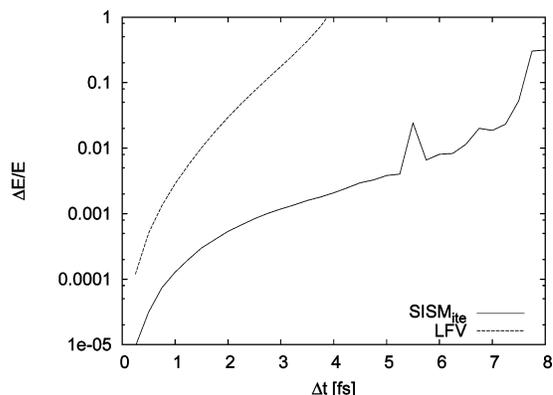
^a Experimental.²⁸ ^b Theoretical.³⁰

Table 4. Parameters of Hamiltonian (28) for SO₂ Molecule³⁷

parameter	value
$b_{OS_0} = b_0$	1.434 Å
θ_0	119.5°
$k_{b_{OS}} = k_b$	1520.0 kcal/mol/Å ²
k_θ	325.0 kcal/mol/radian ²
$e_{O_1} = e_1$	-0.2353125 e_0
$e_S = e_2$	0.4706250 e_0
$e_{O_2} = e_3$	-0.2353125 e_0
σ_{OO}	3.005 Å
σ_{SS}	3.615 Å
ϵ_{OO}	0.11414 kcal/mol
ϵ_{SS}	0.28981 kcal/mol

the force-shifted potential³² with a cutoff distance $r_{\text{off}} = 8.5$ Å.³³ The Lennard-Jones interactions were shifted by adding the term $C_{ij}r_{ij}^6 + D_{ij}$ to the potential, where C_{ij} and D_{ij} were chosen such that the potential and force are zero at $r_{ij} = r_{\text{off}}$.³⁴ The initial positions and velocities of the atoms were chosen at random. The system was then equilibrated for 50 ps where the velocities were scaled every 1000 integration time steps, followed by an additional 50 ps of equilibration at constant energy of the system to ensure that the velocities assume the Maxwell distribution at $T = 216.6$ K. To obtain physically and numerically relevant initial conditions to perform the MD simulation of a system of flexible molecules, the equilibration was also monitored using the Vieillard-Baron rotational order parameter.^{35,36}

Sulfur Dioxide (SO₂). The reference bond lengths and angles as well as the Lennard-Jones potential constants and partial atom charges are taken from refs 37 and 38 for the case of polar SO₂ in liquid state. The bond stretching and angle bending force constants given in Table 4 are obtained in the same way as in the case of CO₂ using the data from Table 3. All other parameters of Hamiltonian (28) are reported in Table 4. We have performed the MD simulation of liquid SO₂ with the density $\rho = 1.20$ g/cm³ at $T = 350$ K.²⁸ The simulation box size for the system composed of 1024 molecules is $a = 45.0$ Å. The simulation protocol is the same as for the liquid CO₂.

**Figure 2.** The error in the total energy of the system of 1024 CO₂ molecules with $\rho = 1.179$ g/cm³ at $T = 216.6$ K using the iterative SISM and LFV for $M = 1000$.

6. RESULTS AND DISCUSSION

To demonstrate the effectiveness of the iterative SISM, we have monitored in all our numerical experiments the error in total energy, $\Delta E/E$, defined as

$$\frac{\Delta E}{E} = \frac{1}{M} \sum_{k=1}^M \left| \frac{E_0 - E_k}{E_0} \right| \quad (43)$$

where E_0 is the initial energy, E_k is the total energy of the system at the integration step k , and M is the total number of integration steps, and compared the results with the corresponding results obtained by the standard LFV algorithm.²³

The error in total energy for the system of CO₂ molecules is depicted in Figure 2 for the iterative SISM and LFV. The period for the antisymmetric stretching of the bond between the carbon and the oxygen atom in the CO₂ molecule is 13.8 fs (see Table 1). We estimate therefore that the maximal acceptable size of the integration time step for the LFV to be 1.0 fs. From results in Figure 2 we conclude that the error in total energy for a 3.0 fs integration time step for the iterative SISM corresponds to the error in the total energy using a 1.0 fs integration time step in the case of the LFV. This means the iterative SISM allows to use up to three times longer time step than the LFV for the same level of accuracy.

The error in total energy for the iterative SISM and LFV for the system of SO₂ molecules is shown in Figure 3. For the iterative SISM using a 4.25 fs integration time step this error roughly corresponds to the error in total energy for the LFV using a 1.0 fs integration time step. Therefore, the iterative SISM for this system allows for using up to a four times longer time step than the LFV for the same level of accuracy.

The actual speed-up of the new method is determined by measuring the required CPU time per integration step. The CPU times for the three methods (the iterative SISM, SISM from ref 10, and LFV) for 1000 MD steps measured on an AMD Opteron 1.6 GHz processor for different system sizes (n molecules) and equal integration time step size (1 fs) are given in Tables 5 and 6 for the systems of liquid CO₂ and SO₂, respectively. The results for both molecular systems show that the computation cost per integration step is almost

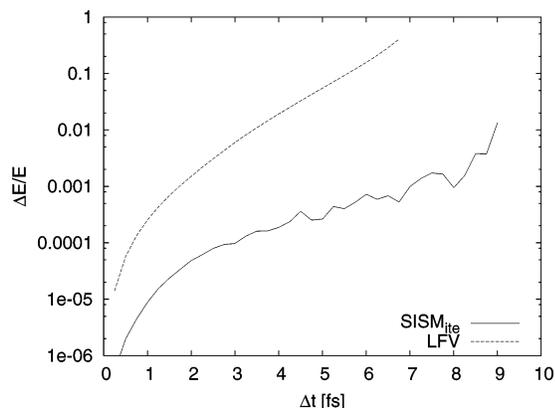


Figure 3. The error in the total energy of the system of 1024 SO_2 molecules with $\rho = 1.20 \text{ g/cm}^3$ at $T = 350 \text{ K}$ using the iterative SISM and LFV for $M = 1000$.

Table 5. CPU Time [s] for Iterative SISM (SISM_{ite}), SISM,¹⁰ and LFV for 1000 MD Steps Measured on an AMD Opteron 1.6 GHz Processor for Different System Sizes (n CO_2 Molecules) and Equal Integration Time Step Size (1 fs)

n	$t(\text{SISM}_{\text{ite}})$ [s]	$t(\text{SISM})$ [s]	$t(\text{LFV})$ [s]	$t(\text{SISM}_{\text{ite}})/$ $t(\text{SISM})$	$t(\text{SISM}_{\text{ite}})/$ $t(\text{LFV})$	$t(\text{SISM})/$ $t(\text{LFV})$
32	2.8	2.6	2.0	1.08	1.40	1.30
64	9.5	9.1	7.8	1.04	1.22	1.17
128	34.2	33.3	31.0	1.03	1.10	1.07
256	130.6	128.4	123.8	1.02	1.05	1.04
512	510.9	504.1	495.1	1.01	1.03	1.02
1024	2009.7	1980.0	1963.4	1.01	1.02	1.01

Table 6. CPU Time [s] for Iterative SISM (SISM_{ite}), SISM,¹⁰ and LFV for 1000 MD Steps Measured on an AMD Opteron 1.6 GHz Processor for Different System Sizes (n SO_2 Molecules) and Equal Integration Time Step Size (1 fs)

n	$t(\text{SISM}_{\text{ite}})$ [s]	$t(\text{SISM})$ [s]	$t(\text{LFV})$ [s]	$t(\text{SISM}_{\text{ite}})/$ $t(\text{SISM})$	$t(\text{SISM}_{\text{ite}})/$ $t(\text{LFV})$	$t(\text{SISM})/$ $t(\text{LFV})$
32	2.5	2.3	1.7	1.09	1.47	1.35
64	8.1	7.6	6.4	1.07	1.27	1.19
128	28.7	27.8	25.4	1.03	1.13	1.09
256	107.6	105.9	101.0	1.02	1.07	1.05
512	417.5	413.9	403.6	1.01	1.03	1.03
1024	1630.3	1628.5	1614.6	1.00	1.01	1.01

the same for the iterative SISM and the SISM from ref 10 while slightly larger than for the LFV. However, for larger systems consisting of more than 1000 atoms the computation cost per integration step becomes approximately the same for all the methods because the time-consuming n^2 numerical calculation of nonbonded forces, which is performed by all three methods in the same way, prevails over the additional calculations in the iterative SISM that scale linearly with n . Therefore, the speed-up of the iterative SISM over the LFV is determined mainly by the significant difference in the integration time step size.

7. CONCLUSIONS

In the present work we combined the standard theory of molecular vibrations with MD integration to derive the iterative SISM, a variation of the SISM developed in ref 10. We explored an alternative approach for the internal coordinate system prediction, which is here made halfway through the integration step. An iterative procedure is then applied to predict the internal coordinate system of a given molecule at the end of the integration step.

The presented method was tested on systems of 1024 molecules of liquid CO_2 and SO_2 . The results show that due to introduction of the moving internal coordinate system, which enables the analytical treatment of high-frequency motions, the iterative SISM allows up to four times longer integration time steps than the standard LFV algorithm for the same level of accuracy, a 4-fold simulation speed-up. Further improvements in efficiency were achieved by implementing the method on computers with highly parallel architecture.^{39,40}

At the present stage of development the new integrator is applicable only to systems of molecules with one equilibrium configuration and no internal rotation. Applying the iterative SISM to molecules with more equilibrium configurations and/or internal rotations, e.g. proteins, is very difficult because additional internal coordinate systems should be introduced to describe each molecular internal rotational degree of freedom.^{1,4,41–45} It would be challenging to develop such an approach and explore its advantages and limitations.

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