Enhancing energy conserving methods*

Sebastian Reich
Konrad-Zuse Zentrum Berlin
Heilbronner Str. 10
D-10711 Berlin

January 9, 1995

Abstract

Recent observations [5] indicate that energy-momentum methods might be better suited for the numerical integration of highly oscillatory Hamiltonian systems than implicit symplectic methods. However, the popular energy-momentum method, suggested in [3], achieves conservation of energy by a global scaling of the force field. This leads to an undesirable coupling of all degrees of freedom that is not present in the original problem formulation. We suggest enhancing this energy-momentum method by splitting the force field and using separate adjustment factors for each force. In case that the potential energy function can be split into a strong and a weak part, we also show how to combine an energy conserving discretization of the strong forces with a symplectic discretization of the weak contributions. We demonstrate the numerical properties of our method by integrating particles that interact through Lennard-Jones potentials.

Keywords: Hamiltonian differential equations, energy-momentum methods, reversible methods, symplectic methods, implicit methods.

AMS(MOS) Subject Classifications: 65L20

CR Subject Classifications: G.1.3

1 Introduction

In this paper we consider numerical integration of Hamiltonian systems

$$\begin{aligned} \frac{d}{dt}q &= M^{-1}p \\ \frac{d}{dt}p &= -\nabla V(q) \end{aligned} \tag{1}$$

with M the diagonal mass matrix, $q, p \in R^n$, and $V : R^n \to R$ the potential energy function.

The solutions of (1) possess a rich geometric structure characterized by the various invariants of (1) [11]. To name just a few: First integrals related to symmetries of (1) such as the Hamiltonian (energy)

$$H(q,p) \;=\; \frac{p^{\mathrm{T}} M^{-1} p}{2} + V(q)$$

and integral invariants related, for example, to the symplectic structure [11]

$$dq \wedge dp \;:=\; \sum_i dq_i \wedge dp_i \tag{2}$$

*This work was partly supported by NIH Grant P41RR05969, DOE/NSF Grant DE-FG02-91-ER25099/DMS-9304268, and NSF GCAG/HPCC ASC-9318159.

of phase space. In addition to this, the solutions of (1) are also known to be time-reversible [11].

It seems natural to ask for numerical schemes that maintain as many invariants of (1) as possible. Recently, so called symplectic integrators have drawn a lot of attention [14]. Symplectic integrators preserve all integral invariants related to the wedge product (2) exactly. However, due to a result by Ge and Marsden [4], those integrators cannot, in general, also preserve energy exactly. Thus, a second option is to consider energy conserving schemes [11],[6],[15].

If one wants to resolve all the details in the motion of (1), explicit symplectic integrators, such as Verlet [16]

$$\begin{aligned} q_{n+1} &= q_n + \Delta t M^{-1} p_{n+1/2} \\ p_{n+1/2} &= p_n - \frac{\Delta t}{2} \nabla V(q_n) \\ p_{n+1} &= p_{n+1/2} - \frac{\Delta t}{2} \nabla V(q_{n+1}) \end{aligned} \tag{3}$$

seem preferable. They show excellent long-time behavior, approximately preserve energy over long periods of time, and are computational inexpensive. In contrast to this, energy conserving schemes are, in general, implicit. But, upon being time-reversible, they exhibit the same excellent long-time behavior as symplectic methods.

The situation differs for Hamiltonian systems containing a strong potential force. For example, consider the Hamiltonian

$$H(q,p) = \frac{p^{\mathrm{T}} M^{-1} p}{2} + U(q) + \frac{g(q)^T K g(q)}{2} \tag{4}$$

with $||K^{-1}|| \ll 1$. Here $U : R^n \to R$, $g : R^n \to R^m$ and K a positive definite $m \times m$ matrix. The corresponding equations of motion are

$$\begin{aligned} \frac{d}{dt} q &= M^{-1} p \\ \frac{d}{dt} q &= -\nabla U(q) - g_q(q)^{\mathrm{T}} K g(q) \end{aligned} \tag{5}$$

Such systems arise, for example, in molecular dynamics simulations [1]. Often one is only interested in the behavior of (5) on time-scales that are much longer than $\sqrt{||K^{-1}||}$. Then explicit integrators with their inherent step-size restriction $\Delta t \ll \sqrt{||K^{-1}||}$ can become rather inefficient and one might want to consider implicit methods instead. Again, one can either choose an implicit symplectic method or an implicit time-reversible energy conserving method. The most well-known family of implicit symplectic integrators are the Gauss-Legendre Runge-Kutta methods [14],[8]. However, when applied to a system of type (5), they suffer from order reduction [7] and instability due to resonance [10]. Thus it seems worthwhile to look at energy conserving methods such as, for example, the following modification of the implicit midpoint rule [3]

$$\begin{aligned} q_{n+1} &= q_n + \Delta t M^{-1} \frac{p_{n+1} + p_n}{2} \\ p_{n+1} &= p_n - \sigma \Delta t \nabla V(\frac{q_{n+1} + q_n}{2}) \end{aligned} \tag{6}$$

with $\sigma \in R$ chosen such that

$$H(q_{n+1}, p_{n+1}) = H(q_n, p_n)$$

(Here we assume that V represents the total potential energy.)

It has been demonstrated that this method has better stability properties than the symplectic midpoint rule [15],[5]. However, the parameter σ introduces a global coupling between all degrees of freedom that cannot be motivated physically. We suggest therefore a modification of (6) that still preserves energy but avoids introducing artificial coupling between all degrees of freedom.

To be more specific: In Section 2, we give a brief analysis of the method (6) and demonstrate that the global coupling through the parameter σ is indeed undesirable. In Section 3, we show how to enhance the method (6) such that no artificial global coupling is introduced through scaling. Often it is possible to split the potential energy function V into a strong part V_{hard} and a weak part V_{soft}. For example, for the Hamiltonian (4), the corresponding splitting would be $V_{\text{soft}}(q) = U(q)$ and

$$V_{\text{hard}}(q) = \frac{g(q)^{\mathrm{T}} K g(q)}{2}.$$

It makes sense to discretize the strong part of the potential by an energy conserving method and the weak contributions by an explicit symplectic method like (3). In Section 4, we show how this can be achieved in practice. Finally, in Section 5, we demonstrate the good stability behavior of our method by means of a simple simulation of particles that interact through Lennard-Jones potentials [16].

A completely different approach to the integration of a system like (5) is to average over the fast degrees of motion and to derive an approximation to the slowly varying components of (5) in terms of a constrained Hamiltonian system [13].

2 An energy conserving method

The modified implicit midpoint rule (6) where σ is chosen to exactly conserve energy was first proposed by Chorin et al. [3]. With $V(q)$ as total potential energy, we require that

$$\frac{p_{n+1}^{\mathrm{T}} M^{-1} p_{n+1}}{2} + V(q_{n+1}) = \frac{p_n^{\mathrm{T}} M^{-1} p_n}{2} + V(q_n),$$

or equivalently

$$\frac{1}{2}(p_{n+1} - p_n)^{\mathrm{T}} M^{-1}(p_{n+1} + p_n) = V(q_n) - V(q_{n+1}).$$

Substituting from eq. (6), we get

$$\sigma \nabla V\left(\frac{q_{n+1} + q_n}{2}\right)^{\mathrm{T}}(q_{n+1} - q_n) = V(q_{n+1}) - V(q_n).$$

Using this equation to eliminate σ from eq. (6) gives

$$\begin{aligned} q_{n+1} &= q_n + \Delta t M^{-1} \frac{p_{n+1} + p_n}{2} \\ p_{n+1} &= p_n - \Delta t \frac{V(q_{n+1}) - V(q_n)}{\nabla V(\frac{1}{2}q_{n+1} + \frac{1}{2}q_n)^{\mathrm{T}}(q_{n+1} - q_n)} \nabla V\left(\frac{q_{n+1} + q_n}{2}\right) \end{aligned} \tag{7}$$

This method has the disturbing feature of making equal adjustments to all forces regardless of which interactions are most responsible for the energy error. For example, let us assume that there is a coordinate splitting $q = (q_1^T, q_2^T)^T$ such that the the potential energy V can be written as

$$V(q) = V^1(q_1) + V^2(q_2).$$

Then the motions in q_1 and q_2 are clearly decoupled and independent of each other. However, in the discretization (7) these motions become linked together through the common scaling factor σ. This coupling becomes even more pronounced if one looks at the following modification of the midpoint rule

$$\begin{aligned} q_{n+1} &= q_n + \sigma \Delta t M^{-1} \frac{p_{n+1} + p_n}{2} \\ p_{n+1} &= p_n - \Delta t \nabla V\left(\frac{q_{n+1} + q_n}{2}\right) \end{aligned}$$

with σ again chosen such that total energy is conserved. This method preserves now energy by a simple scaling of all velocities by a factor σ. Although this approach is sometimes used in molecular dynamics simulations to keep the kinetic energy (or total energy) constant [1], it is also well-known that such a scaling can lead to non-physical artifacts in the numerical results.

The modified method (7) automatically preserves linear and angular momentum [5]. Therefore, (7) is sometimes called an energy-momentum method [11]. Higher-order time-reversible and energy conserving schemes can be obtained, for example, by a proper modification of higher-order Gauss-Legendre Runge Kutta methods [8]. For example, one could modify a method of order $2s$ with Butcher Tableau [7]

$$\begin{array}{cc} c & A \\ & b^{\mathrm{T}} \end{array}$$

to

$$\begin{aligned} q_{n+1} &= q_n + \Delta t M^{-1} \sum_i b_i P_i \\ p_{n+1} &= p_n - \sigma \Delta t \sum_i b_i \nabla V(Q_i) \end{aligned}$$

and, for $j = 1, \ldots, s$,

$$\begin{aligned} Q_j &= q_n + \Delta t M^{-1} \sum_i a_{ij} P_i \\ P_j &= p_n - \sigma \Delta t \sum_i a_{ij} \nabla V(Q_i) \end{aligned}$$

such that total energy is conserved. Formally we have

$$\sigma = \frac{V(q_{n+1}) - V(q_n)}{\Delta t (p_{n+1} + p_n)^T M^{-1} \sum b_i \nabla V(Q_i)}$$

which makes the scheme now also implicit in q_{n+1} and p_{n+1}. Again, this leads to a global coupling of all degrees of freedom.

3 An enhanced energy conserving method

The method (7) makes equal adjustments to all the forces regardless of which interactions are most responsible for the energy error. We can try to localize the effects of these adjustments by splitting the potential energy

$$V(q) = \sum_k V^k(q)$$

and hence the force terms and using separate adjustment factors for each force:

$$-\sigma_1 \nabla V^1 - \sigma_2 \nabla V^2 - \cdots - \sigma_m \nabla V^m .$$

Each σ_k is determined by the formula

$$\sigma_k = \frac{V^k(q_{n+1}) - V^k(q_n)}{\nabla V^k(\frac{1}{2} q_{n+1} + \frac{1}{2} q_n)^{\mathrm{T}} (q_{n+1} - q_n)},$$

which ensures that the energy would be exactly conserved in the absence of all forces except $-\nabla V^k$ and which keeps the scheme time-reversible. This method is just as implicit as the midpoint rule but it has the nice feature of also conserving total energy. To see this note that conservation of total energy requires

$$\begin{aligned} V(q_{n+1}) - V(q_n) &= -\frac{1}{2}(p_{n+1}-p_n)^{\mathrm{T}} M^{-1}(p_{n+1}+p_n) \\ &= \sum_k \sigma_k \nabla V^k(\frac{q_{n+1}+q_n}{2})^{\mathrm{T}}(q_{n+1}-q_n) \\ &= \sum_k V^k(q_{n+1}) - V^k(q_n) \end{aligned}$$

Since all the σ_k's obviously satisfy

$$\sigma_k = 1.0 + O(\Delta t)$$

and the method is time-reversible, the scheme is of second order in (q,p). For linear Hamiltonian systems we have $\sigma_k = 1.0$. Thus, the factor $|\sigma_k - 1.0|$ reflects the nonlinearity in (1) due to the force $-\nabla V^k$.

Example. For a two-body interaction like $V^k(q) = \frac{1}{2}\phi(\|r_j - r_i\|^2)$, its force $-\nabla V^k$ is

$$-\phi'(\|r_{ij}\|^2)\begin{bmatrix} 0 \\ r_{ij} \\ 0 \\ -r_{ij} \\ 0 \end{bmatrix}$$

with $r_{ij} = r_i - r_j$. It can be seen that if we push the splitting for particle systems with two-body interactions to these most elementary interactions, then we require no force evaluation at the midpoint due to cancellation of ϕ' in the numerator and denominator. (See Section 5 for a concrete example.) The resulting method can then be shown to be equivalent to a particular scheme proposed in [6] where energy conserving methods for systems of particles interacting through distance-dependent potentials were considered.

Example. Consider the nonlinear wave equation

$$\begin{aligned} \frac{d}{dt}q &= p \\ \frac{d}{dt}p &= -q_{xx} - \nabla U(q) \end{aligned}$$

on $[0, 2\pi]$ with periodic boundary conditions. An example is the Sine-Gordon equation where $U(q) = \sin(q)$. After spatial discretization by a finite-difference method, we obtain

$$\begin{aligned} \frac{d}{dt}q &= p \\ \frac{d}{dt}p &= -Aq - \sum_i \nabla U(q_i) \end{aligned}$$

with $A \in R^N \times R^N$ the discrete Laplacian and $q = (q_1, q_2, \ldots, q_N)^T$, $p = (p_1, p_2, \ldots, p_N)^T$. The corresponding potential energy function is

$$V(q) = \frac{q^T A q}{2} + \sum_i U(q_i)$$

which can be split into

$$V^0(q) = \frac{q^T A q}{2}$$

and

$$V^k(q) = U(q_k)$$

$k = 1, \ldots, N$. For V^0 the corresponding σ_0 satisfies $\sigma_0 = 1.0$.

If the kinetic energy and each entry V^k in the total potential energy are invariant under a symmetry group acting on (q, p) by extended point transformation [11], then the corresponding momentum map $J(q, p)$ is preserved by our enhanced energy method. This follows from the fact that the momentum map can be written as [12]

$$J(q,p) = q^{\mathrm{T}} W p$$

where W is a constant $n \times n$ matrix, and that

$$q^{\mathrm{T}} W \nabla V^k(q) = 0$$

as well as

$$p^{\mathrm{T}} M^{-1} W p = 0.$$

Thus

$$q_{n+1/2}^{\mathrm{T}} W \sum_k \sigma_k \nabla V^k(q_{n+1/2}) = 0$$

and

$$p_{n+1/2}^{\mathrm{T}} M^{-1} W p_{n+1/2} = 0$$

and it follows, after a little bit of linear algebra [12], that

$$q_{n+1}^{\mathrm{T}} W p_{n+1} = q_n^{\mathrm{T}} W p_n .$$

Here we used the notations $q_{n+1/2} = (q_{n+1} + q_n)/2$ and $p_{n+1/2} = (p_{n+1} + p_n)/2$. Thus, the enhanced method also conserves, for example, linear and angular momentum.

Again higher-order methods can be obtained, for example, by extending the idea of splitting the force field to higher-order Gauss-Legendre Runge-Kutta methods as described in Section 2 for the single parameter case. This time we would have to chose the σ_k's such that

$$\sigma_k = \frac{V^k(q_{n+1}) - V^k(q_n)}{\Delta t (p_{n+1} + p_n)^T M^{-1} \sum b_i \nabla V^k(Q_i)} .$$

Remark. La Budde and Greenspan [9] used a similar splitting of the force field to derive higher-order energy conserving methods based on the Adams' formulae and Taylor series methods. However, they considered only forces that are pairwise-additive functions of the distances r_{ij} between particles. This is rather restrictive. Since, for example, force fields used in molecular dynamics simulations have more complicated dependencies (for example, on bond angles and torsion angles [1]). In addition, their schemes do not preserve angular momentum exactly and are not time-reversible in general.

4 Combining symplectic and energy conserving methods

Let us first rewrite our enhanced energy-momentum method as

$$\begin{aligned}
q_{n+1} &= q_n + \Delta t M^{-1} p_{n+1/2} \\
p_{n+1/2} &= p_n - \frac{\Delta t}{2} \sum_k \sigma_k \nabla V^k \left(\frac{q_{n+1} + q_n}{2}\right) \\
p_{n+1} &= p_{n+1/2} - \frac{\Delta t}{2} \sum_k \sigma_k \nabla V^k \left(\frac{q_{n+1} + q_n}{2}\right)
\end{aligned}$$

with the σ_k's chosen as before. Then, assuming that we have a splitting of the potential V into a strong and weak contribution as described in Sections 1, we can combine our method with the explicit Verlet method

enhanced energy-momentum method	$\Delta t = 20$ fsec	$\langle E_{\text{kin}}\rangle = 90.3$	$\langle(\Delta E_{\text{kin}})^2\rangle^{1/2} = 28.7$
	$\Delta t = 50$ fsec	$\langle E_{\text{kin}}\rangle = 90.8$	$\langle(\Delta E_{\text{kin}})^2\rangle^{1/2} = 27.1$
	$\Delta t = 100$ fsec	$\langle E_{\text{kin}}\rangle = 90.9$	$\langle(\Delta E_{\text{kin}})^2\rangle^{1/2} = 27.1$
	$\Delta t = 200$ fsec	$\langle E_{\text{kin}}\rangle = 92.3$	$\langle(\Delta E_{\text{kin}})^2\rangle^{1/2} = 26.4$
	$\Delta t = 500$ fsec	$\langle E_{\text{kin}}\rangle = 94.2$	$\langle(\Delta E_{\text{kin}})^2\rangle^{1/2} = 26.8$
Verlet method	$\Delta t = 20$ fsec	$\langle E_{\text{kin}}\rangle = 90.0$	$\langle(\Delta E_{\text{kin}})^2\rangle^{1/2} = 27.8$

Table 1: Average kinetic energy and its standard deviation computed with our enhanced energy-momentum method compared to the values obtained by the Verlet method.

(3) to obtain

$$\begin{aligned}
q_{n+1} &= q_n + \Delta t M^{-1} p_{n+1/2} \\
p_{n+1/2} &= p_n - \frac{\Delta t}{2}\sum_k \sigma_k \nabla V^k_{\text{hard}}(\frac{q_{n+1}+q_n}{2}) - \frac{\Delta t}{2}\nabla V_{\text{soft}}(q_n) \\
p_{n+1} &= p_{n+1/2} - \frac{\Delta t}{2}\sum_k \sigma_k \nabla V^k_{\text{hard}}(\frac{q_{n+1}+q_n}{2}) - \frac{\Delta t}{2}\nabla V_{\text{soft}}(q_{n+1})
\end{aligned}$$

The method is time-reversible, preserves angular momentum exactly, and has the same energy conserving properties as the Verlet method applied to a smooth problem and using a small step-size. The combined method has the advantage that the force field $-\nabla V_{\text{soft}}$ enters the discretization explicitly and thus reduces the computational costs of the overall method significantly. (For example, in molecular dynamics simulations without cut-off, up to 90 % of the interparticle forces are weak forces in the above sense.)

5 Numerical Example

As a numerical test example we simulated a two-dimensional frozen argon crystal. We used the same configuration as described in [2]; i.e., six argon atoms arranged symmetrically around a center atom with Lennards-Jones potential between each atom pair. The potential energy of the system is

$$V(q) = \frac{1}{2}\sum_{i=1}^{6}\sum_{j=i+1}^{7} \phi(||r_j - r_i||^2)$$

where

$$\phi(r^2) = 8\epsilon\left(\left(\frac{\delta}{r}\right)^{12} - \left(\frac{\delta}{r}\right)^{6}\right).$$

Recall that $q = (r_1^{\text{T}}, r_2^{\text{T}}, \ldots, r_7^{\text{T}})^{\text{T}}$ and each $r_i \in R^2$, $i = 1, 2, \ldots, 7$.

For the simulation we took $\epsilon = 0.2383\,\text{kcal/mol}$, $\delta = 3.405\,\text{Å}$, and particle mass $m = 39.95\,\text{amu}$. The initial positions of the particles are slightly perturbed about those for lowest potential energy. They are given low initial velocities such that the total momentum of the system is zero and the initial temperature is 22.72 K [2].

The system was simulated using our enhanced energy-method method of Section 4. The simulation was run for a time of $t_{\text{tot}} = 1.0$ nanosecond. The computed average kinetic energy $\langle E_{\text{kin}}\rangle$ and its standard deviation $\langle(\Delta E_{\text{kin}})^2\rangle^{1/2} = \langle(E_{\text{kin}} - \langle E_{\text{kin}}\rangle)^2\rangle^{1/2}$ for step-sizes increasing from 20 to 500 femtoseconds are given in Table 1 and compared to the values obtained by using the Verlet method with a step-size of 20 femtoseconds.

We defined the potential V_{hard} by including all the nearest neighborhood interactions. The remaining (far-distance) terms were collected in the potential V_{soft}. The potential V_{hard} was then split into its elementary two-particle interactions.

To demonstrate how we solved the resulting nonlinear system of equations in (q_{n+1}, p_{n+1}), let us assume, for simplicity, that we do not split the potential energy function V and apply our enhanced energy conserving scheme to all the two-particle interactions. We obtain

$$\begin{aligned} q_{n+1} &= q_n + \Delta t M^{-1} \frac{p_{n+1} + p_n}{2} \\ p_{n+1} &= p_n - \frac{\Delta t}{2} \sum_{i=1}^{6} \sum_{j=i+1}^{7} \frac{\phi(r_{ij,n+1}) - \phi(r_{ij,n})}{||r_{ij,n+1}||^2 - ||r_{ij,n}||^2} \begin{bmatrix} 0 \\ r_{ij,n+1} + r_{ij,n} \\ 0 \\ -r_{ij,n+1} - r_{ij,n} \\ 0 \end{bmatrix} \end{aligned}$$

with $r_{ij} = r_i - r_j$. We can solve this nonlinear system of equations by using the following iteration

$$\begin{aligned} q_{n+1}^{l+1} &= q_n + \Delta t M^{-1} \frac{p_{n+1}^{l+1} + p_n}{2} \\ p_{n+1}^{l+1} &= p_n - \frac{\Delta t}{2} \sum_{i=1}^{6} \sum_{j=i+1}^{7} \frac{\phi(r_{ij,n+1}^{l}) - \phi(r_{ij,n})}{||r_{ij,n+1}^{l}||^2 - ||r_{ij,n}||^2} \begin{bmatrix} 0 \\ r_{ij,n+1}^{l+1} + r_{ij,n} \\ 0 \\ -r_{ij,n+1}^{l+1} - r_{ij,n} \\ 0 \end{bmatrix} \end{aligned} \tag{8}$$

$l = 0, 1, \ldots$, which requires the solution of a linear system of equations in each iteration. As a starting value we take

$$q_{n+1}^0 = q_n + \Delta t M^{-1} p_n .$$

Note that this implementation preserves angular momentum in each iteration and can easily be extended to the combined method of Section 4.

For step-sizes larger than 100 femtoseconds we had to use a damped version of the above iteration. For that reason we first computed

$$\Delta q_{n+1}^{l+1} := q_{n+1}^{l+1} - q_{n+1}^{l}$$

with q_{n+1}^{l+1} obtained from the linear system (8) and then used

$$q_{n+1}^{l+1} := q_{n+1}^{l} + \alpha \Delta q_{n+1}^{l+1}$$

with properly chosen $\alpha \in \{1, 1/2, 1/4, \ldots\}$ in the next iteration.

The Verlet method started to show significant deviations in total energy for step-sizes larger than 50 femtoseconds. This agrees with the results given in [2]. Although we observed a slightly higher average kinetic energy for larger step-sizes, our method remained stable for step-sizes $\Delta t > 50$ femtoseconds and there was no drift in the kinetic or potential energy. However, to gain an effective speed-up in terms of CPU-time and to allow for step-sizes $\Delta t > 500$ femtoseconds, a more sophisticated iterative solver for the nonlinear equations and its careful implementation are needed. This will be discussed in a forthcoming paper.

6 Acknowledgement

This work was initiated while the author was visiting T. Schlick and R.D. Skeel at the Courant Institute, New York.

References

[1] M.P. Allen and T.J. Tildesley, *Computer simulation of liquids*, Clarendon Press, Oxford, 1987.

[2] J.J. Biesiadecki and R.D. Skeel, Danger of multiple-time-step methods, *J. Comput. Phys.* **109**, 318–328, 1993.

[3] A.J. Chorin, T.J.R. Hughes, J.E. Marsden and M. McCracken, Product formulas and numerical algorithms, *Comm. Pure and Appl. Math.* **31**, 205–256, 1979.

[4] Z. Ge and J.E. Marsden, Lie-Poisson integrators and Lie-Poisson Hamiltonian-Jacobi theory, *Phys. Lett. A* **133**, 134-139, 1988.

[5] O. Gonzales and J.C. Simo, On the stability of symplectic and energy-momentum algorithms for non-linear Hamiltonian systems with symmetry, Techn. Report, Stanford Univ., 1994.

[6] D. Greenspan, Conservative numerical methods for $\ddot{x} = f(x)$, *J. Comput. Phys.* **56**, 28–41, 1984.

[7] E. Hairer and L. Jay, Implicit Runge-Kutta methods for higher index differential-algebraic systems, In: *Contributions in numerical mathematics.*, *WSSIAA* **2**, 213–224, 1993.

[8] E. Hairer, S.P. Norsett and G. Wanner, Solving ODEs. I, 2nd edition, Springer Verlag, 1993.

[9] R.A. La Budde and D. Greenspan, Energy and momentum conserving methods. II, *Numer. Math.* **26**, 1–16, 1976.

[10] M. Mandziuk and T. Schlick, Resonance in the dynamics of chemical systems simulated by the implicit midpoint scheme, Techn. Report, Courant Institute, 1994.

[11] J.E. Marsden, *Lectures on mechanics*, Cambridge University Press, 1992.

[12] S. Reich, Momentum conserving symplectic integrators, *Physica D* **76**, 375–383, 1994.

[13] S. Reich, Smoothed dynamics of highly oscillatory Hamiltonian systems, submitted, 1994.

[14] J.M. Sanz-Serna, Symplectic integrators for Hamiltonian problems: An overview, *Acta Numerica* **1**, 243–286, 1991.

[15] J.C. Simo and N. Tarnow, The discrete energy-momentum method. Conserving algorithms for nonlinear elastodynamics, *ZAMP* **43**, 757–793, 1992.

[16] L. Verlet, Computer 'experiments' on classical fluids. I. thermodynamical properties of Lennard-Jones molecules, *Phys. Rev.* **159**, 98–103, 1967.