Symplectic Integration of Classical Trajectories: A Case Study

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Classical trajectory calculations for a triatomic, complex forming system are used to assess the effectivity (correctness at given computational expense) of new, symplectic integrators of sixth and fourth orders (S6 and S4) compared to a traditional predictor−corrector scheme of sixth order (G). With respect to energy conservation and positional error, S6 is two to three orders better than G, while S4 is no improvement. However, comparison with quadruple precision calculations shows that even with S6 the correct computation in double precision arithmetic is limited to trajectory lifetimes of about 25 typical molecular vibrations. Moreover, in contrast to common assumptions, even energy conservation to 10^{-12} does not guarantee that the trajectory is correct, or even that it reaches the correct reaction channel.

1. Introduction

The computation of classical trajectories[1,2] simulating molecular scattering on a given potential is sometimes regarded as a trivial problem. This may be so for the simulation of direct collisions, where today we have enough computer power to run millions of trajectories in a few hours, especially if we take their correctness for granted if only energy conservation holds to 10^{-6}. But even for direct collisions, situations exist where the evaluation of one integration step is so expensive that one is grateful for any improvement in the numerical integration routine. This is, e.g., the case in AIMD (ab initio molecular dynamics) (see ref 3; cf. also ref 4], where at each integration step the potential derivative is computed ab initio.

The situation is very different if we want to simulate long-lived, complex collisions or unimolecular decay. Here, the trajectories are necessarily long (in terms of a typical vibrational period of the system), and the question of how accurate they are is usually just repressed. Correctness is generally assumed if energy is conserved, and few people believe or know that a trajectory can be completely wrong, e.g. emerge as reactive instead of nonreactive, even if energy conservation is better than 10^{-12}.

The invention of a set of new symplectic integrators in our group by Teloy[5] was taken as an opportunity to investigate the accuracy of long-lived trajectories such as those we have computed for many years. "Symplectic", or "canonical", integrators[6,7] are integrating algorithms, for which by construction (ideally, i.e., neglecting rounding errors) each integration step is a symplectic, or canonical, transform. Since the dynamics of Hamiltonian systems, which include molecular scattering, is also symplectic, one expects that they are well-adapted to the integration of such systems. Among other things symplectic dynamics conserves several quantities such as energy, total angular momentum, and phase space volume. With some modifications this holds also (ideally) for numerical symplectic integration. In addition, symplectic integrators may be (and Teloy's are) symmetric under time-reversal.

The Verlet "leapfrog" algorithm popular in molecular dynamics is a symplectic integrator of second order. Higher order symplectic routines are not yet widespread in classical trajectory work,[8,9] though their usefulness has been assessed.[10] However, algorithms of sixth and higher order[11−13] are still rare.

In this, necessarily limited, study we took one symplectic integrator of sixth order, and one of fourth order (abbreviated S6 and S4 in this paper), and compared them with a sixth order predictor−corrector integrator by Gear,[14] which we have used for many years. The latter (abbreviated G here) had been selected 17 years ago on the basis of a comparison[16] with 7 other integrating routines popular at that time (including Runge−Kutta−Lawson (order 5), Runge−Kutta−Fehlberg (6), Rosenbrock (4), a predictor−corrector routine by Hamming (5), and EPISODE (variable order)), which were applied to essentially the same type of problem as now. At the suggestion of one reviewer, we also did a few runs with an integrator from the recent literature, i.e., the sixth order nine-step integrator recommended by McLachlan[13] (abbreviated ML).

The system which we integrate is similar to the scattering of H^+ from D_2; i.e., we use the DIM potential energy surface for H_3^+,[17] but the masses $m_a = m_c \approx 1.73$ u and $m_b \approx 1.56$ u. The system dynamics is chaotic (the usual mixture of regular and chaotic phase space regions), and there are numerous trajectories which are trapped in the potential for many (tens or hundreds or more, depending on energy) vibrational periods.[18,19] Since our aim was to look into the limits of correct integration, we did not integrate a microcanonical ensemble of trajectories but selected 1000 trajectories of different lifetimes from such an ensemble. These were run with different step sizes for a sufficiently large time, fixed for each trajectory in order to allow the comparison not only of conserved quantities (energy, angular momentum) but also of the positions of the final points in phase space. We discarded the alternative of computing and comparing probability *distributions* of simulated "real" reactions, because in this case significant differences can only be obtained with much larger expense.

Since there is no analytic way to know the end points exactly, an assessment of their accuracy is not easy and never completely certain. We used quadruple precision arithmetic[20] with very small integration steps to define what we nominally call the "correct" trajectories. In addition, one must also define what one calls a "better" integrating routine. We used the number

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of substeps, i.e., calls to the potential derivatives (which dominate the expense of the calculation), to define a better integrator as one which needs less substeps to compute a given fraction of correct trajectories.

As a measure for the length, and that implies the complexity, of a trajectory we use the number M of "minimum exchanges" (MEs),[21] defined as the number of changes of the identity of the shortest of the three interatomic distances (R_{AB}, R_{BC}, R_{CA}) in the collision complex. As a dimensionless quantity M is invariant with respect to the scaling of nuclear masses, or potential parameters (well depth, equilibrium distance). Roughly speaking, two MEs correspond to one typical molecular vibration in the complex. For $M > 3$ this number is nearly proportional to the lifetime of the complex. In our example one ME corresponds to about 12.5 fs.

The result of this study is that integrator S6, but not S4, is definitely better than G. In addition, our computations show the incorrectness of some common folklore about classical trajectory computations: Neither good energy conservation nor back integrability are *sufficient* to ensure a correct trajectory, and even with a good integrating routine (which S6 certainly is) the *correct* integration of complex trajectories in a typical triatomic molecular potential well is limited to about 40 MEs (or 20 vibrational periods) in double precision (DP), and perhaps 80 in quadruple precision (QP).

The concept of the paper is as follows: Section II describes the model, section III the integrators and section IV the calculations, and section V presents the detailed results and discusses them.

II. The Model

For this study we used the DIM potential for H_3^+, which we had used in several earlier studies (see refs 18, 19, and 21, and references cited therein). Its exact shape is irrelevant in this study, and from older calculations[22] we know that we could as well have used a triple Morse ansatz. If we measure the duration of a trajectory in units of MEs, energies in units of the well depth, and distances in units of the equilibrium distance of the triatomic well, *all* classical calculations for the same potential shape are equivalent. The only variable which is not automatically scaled in this way is momentum, which we need in the definition of positional errors in phase space. Here we use internal units which ensure that the distance in momentum space and that in position space contribute in a balanced manner to the phase space distance.

The calculation was done with the following physical parameters: Masses $m_a = m_c = 1.7353$ u and $m_b = 1.5625$ u; 3D well depth measured from the first dissociation level 4.924 eV; equilibrium distance of the equilateral complex, 0.9187 Å, resulting in normal mode periods of the order of 25 fs. The collision energy was 1.0 eV. The trajectory lengths in real time units were between 140 and 1600 fs.

III. Integrators

Both symplectic integrators are explicit single-step ordinary differential equation (ODE) solvers and belong to the class of explicit partitioned Runge−Kutta methods in the language of ref 6. S4 is related but not equal to example 8.1 in ref 6. In the language of ref 13 both integrators belong to type S, i.e., are a composition of single symplectic steps. S6 was derived by Teloy[5] with methods similar to those of refs 11−13. Both integrators can be used for any Hamiltonian system whose Hamiltonian can be partitioned, i.e., written as $H = T(\mathbf{p}) + V(\mathbf{q})$. This holds for most coordinate systems in which one would integrate trajectories. The right-hand sides of the differential equations are defined as the vector components $fp_i = -\partial H/\partial q_i$, $fq_i = \partial H/\partial p_i$, and h is the (full) time step. Then one full step of S4 is given by the sequence of fractional substeps

$$\begin{aligned}&\text{do } i = 0, 2, 4, 6, 8\\ &\mathbf{p} = \mathbf{p} + ha(i)\mathbf{fp}\\ &\mathbf{q} = \mathbf{q} + ha(i+1)\mathbf{fq}\\ &\text{end do}\\ &\mathbf{p} = \mathbf{p} + ha(10)\mathbf{fp}\end{aligned} \tag{1}$$

where

$$a(0) = a(10) = {}^1/_2 \qquad a(1) = a(9) = -{}^1/_{48}$$
$$a(3) = a(7) = {}^3/_8$$
$$a(2) = -a(4) = -a(6) = a(8) = {}^1/_3 \qquad a(5) = {}^7/_{24}$$

So we have five substeps, each calling **fp** and **fq** once, plus step 10, which can be combined with step 1 in a calculation of a series of full steps.

Similarly, one full step of S6 is given by

$$\begin{aligned}&\text{do } i = 0, 2, 4, ..., 14, 16\\ &\mathbf{q} = \mathbf{q} + ha(i)\mathbf{fq}\\ &\mathbf{p} = \mathbf{p} + ha(i+1)\mathbf{fp}\\ &\text{end do}\\ &\mathbf{q} = \mathbf{q} + ha(18)\mathbf{fq}\end{aligned} \tag{2}$$

where now the coefficients are no longer analytically known. The numbers given here are exact to 20 digits:

$$a(0) = a(18) = +0.095\,176\,254\,541\,774\,052\,68$$
$$a(1) = a(17) = +0.666\,296\,893\,997\,707\,801\,34$$
$$a(2) = a(16) = -0.127\,950\,285\,523\,686\,779\,41$$
$$a(3) = a(15) = +0.024\,618\,900\,952\,105\,087\,13$$
$$a(4) = a(14) = +0.105\,972\,953\,453\,251\,131\,44$$
$$a(5) = a(13) = -0.410\,725\,533\,617\,951\,132\,32$$
$$a(6) = a(12) = +0.448\,222\,276\,600\,827\,484\,17$$
$$a(7) = a(11) = +0.657\,729\,262\,050\,913\,177\,69$$
$$a(8) = a(10) = -0.021\,421\,199\,072\,165\,888\,87$$
$$a(9) = 2.0 \times -0.437\,919\,523\,382\,774\,933\,84$$

From the sequence of steps and the coefficients it is obvious that both symplectic integrators are explicitly time-reversible. McLachlan's integrator ML, defined in ref 13, is very similar to S6 but with different coefficients.

The stability of the recursions 1 and 2 was determined by applying it to the harmonic oscillator. The maximum stable time step in units of ω, $h\omega$, is $\approx$1.552 for S4 and $\approx$6.363 for S6. This means that S6 allows time steps four times as large as those of S4. The stability of S6 is also much better than that of ML with $h\omega < 2.507$.

The Gear integrator, fully described in ref 14, does not distinguish between **q** and **p**. It has a fifth order predictor and a sixth order corrector. Since it is implicit, it is not self-starting,

and we start it with three Runge−Kutta steps. Normally we have used it with variable step size, but for this study that feature has been switched off. To keep the paper short, the formula is not reproduced here. For the three free parameters of the method we take $a_1 = {}^1/_2$, $a_2 = 1$, and $\beta = {}^9/_{56}$ as recommended by Gear.

IV. Calculations

To start a trajectory, its twelve initial phase space coordinates, and its necessary integration time, which were predetermined in a test run, were read from a file. To compare the end points obtained for different step sizes, each trajectory was finished in all runs at exactly the same fixed time, which was taken as a multiple of the largest time step used. All time steps were reciprocal powers of 2.0 (in terms of the time unit of the program, which is 10 fs) in order to prevent rounding errors of the time variable. In the following we call a time step of 2^{-n} units, i.e., $2^{-n} \times 10$ fs, a time step of size n. For DP computations we used $n = 5...11$ for S6, 6...12 for S4, and 7...13 for G. (That leads to a comparable range of substeps.) Larger values produce increasing errors in DP. For comparison (and not as a recommendation for production runs) we similarly used QP with $n = 5...12$ (and up to 14 in doubtful cases) for S6, 6...13 for S4, and 7...14 for G. During the integration the number of MEs was monitored and together with the end point saved in a file, from which the evaluations were done.

Classical trajectory calculations are generally performed for a microcanonical ensemble of initial conditions, or sometimes a more selective one with defined physical properties. In most cases this leads to a predominance of short-lived trajectories. In this study we were interested in the correctness of long trajectories as a function of their length. Therefore, we took a first, large microcanonical ensemble of scattering trajectories only as the basis, from which we selected 1000 initial conditions in sets of 10, which defined trajectories with (preliminary) ME counts from 0 to 99. With this ensemble all further calculations were done.

A nontrivial problem is the assessment of the final error in a trajectory calculation, when the analytic solution of the differential equations is not known. This question has two sides. For a quantity which is conserved by the system's dynamics it is easy to compare its value at the end of the trajectory with that at its beginning. This holds in our case for energy and total angular momentum. (In principle, also the volume element is conserved. But this is a differential quantity, and a test of its conservation with finite approximations fails due to the enormous distortions of volume elements by the exponential divergence of adjacent trajectories.) In addition, the result of back-integration can be checked easily, since also here the result is known.

The situation is different if we ask for other properties of the trajectory, e.g. its end position, or just the number of minimum exchanges, M. (Note that a simple change of M by one means that the trajectory will generally end in a different reaction channel!) For these kinds of properties the numeric accuracy can only be assessed by comparison with a "more accurate" numerical calculation. This is a logical circle, and the only mathematically acceptable way out would be an interval inclusion of the correct result computed on a computer with correctly rounded interval arithmetic, as we have used in one case.[23] However, this is completely unfeasible here. Therefore, we can only check whether some property practically converges and assume that the seemingly converged property is correct. For the rest of the paper we, therefore, *define* a correct trajectory as one which gives the same number of MEs in three computations with consecutively halved time steps. To check the full range of DP arithmetic, we compared with a QP calculation.[20] In the case of doubt the QP calculation with S6 is taken as the correct one, and for all trajectories with $M < 80$ additional halving steps have been included to ensure apparent convergence. A look into a table of the apparent M vs the step size showed that it is highly improbable (<1%) that after three equal values of M this number changes again after the next halving step. For all but 66 out of 1000 trajectories convergence in the above sense was reached with a stepsize of $n = 14$.

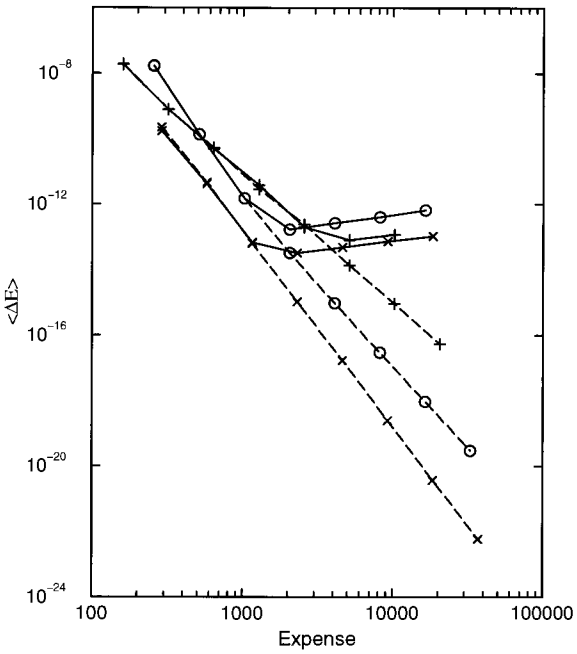

Figure 1. Average final energy deviation (eV) of all trajectories as a function of the expense, i.e., the number of integration substeps per 10 fs. Integrators: ○, G; +, S4; ×, S6. The upper curves are for DP; the lower ones for QP. The straight parts correspond to powers of −4, −5, and −6 for S4, G, and S6, respectively.

V. Results

A. Accuracy of Conserved Quantities. In this case we can take statistical averages over either all trajectories or only those which we consider to be correct, but it turns out that the result is practically the same. In both cases E and L are computed at the beginning and end of the trajectory, and their differences compared. Figure 1 shows the errors ΔE as a function of the "expense", i.e., the number of substeps (calls to the right side of the differential equation). Since every substep means a call to the subroutine computing the potential derivatives, the total computing time is generally dominated by this number. The number of substeps per full integration step is 9, 5, and 2 for S6, S4, and G, respectively. The total number of substeps for a substep size of $2^{-14} \times 10$ fs (the smallest useful substep size in DP) was between 10^4 and 10^7. Figure 1 shows that as long as rounding errors do not counteract, the improvement of the energy error with decreasing stepsize is a power law with powers −4, −5, and −6 for integrators S4, G, and S6, respectively. One sees also that S6 is better than G with respect to ΔE by 2−3 orders of magnitude, which means that it is more than two times faster for a fixed ΔE. S4, due to its low order, is an improvement over G only for very small step sizes. The limitation inherent in the word size of DP is obvious: a ΔE better than 10^{-12} cannot be reached. To avoid

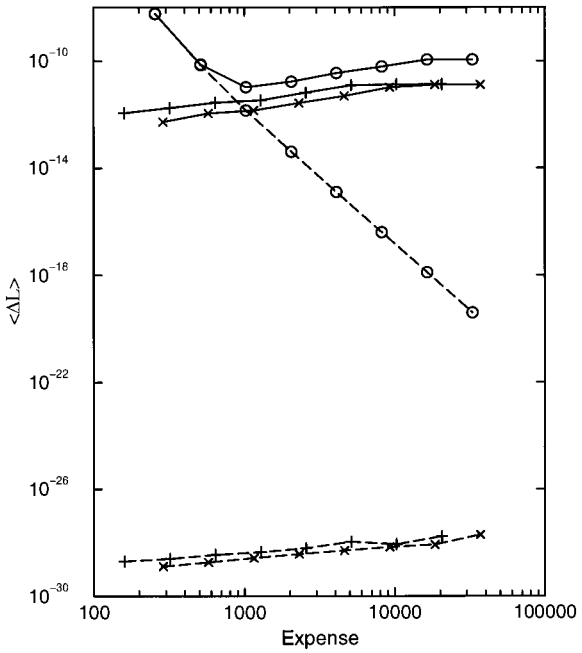

Figure 2. Average final deviations of the total angular momentum (in units of $\hbar$) of all trajectories as function of the expense, i.e., the number of integration substeps per 10 fs. Integrators: ○, G; +, S4, ×, S6. The upper curves are for DP; the lower ones for QP. The straight parts have approximate powers of 1, −5, and 1 for S4, G, and S6, respectively.

overcrowding the figure, five points calculated in DP with integrator ML are not plotted. For step sizes where $\langle \Delta E \rangle$ is ruled by the truncation error (left part of plot) ML has about 30 times larger errors than S6.

We also computed $\sum(E_i - E_{i-1})^2$ averaged over the respective number of integration steps, which is an approximation to the fluctuation of the energy about a local mean. The result is very similar to Figure 1, and not shown.

Figure 2 shows the error, ΔL, of the total angular momentum. Here, an impressive improvement by many orders of magnitude can be seen. For symplectic integration ΔL is practically constant; it remains (with a small linear increase) at the lowest level determined by the word size.

One may wonder why this difference between energy and angular momentum conservation exists, since the exact solution of Hamilton's equations conserves both properties exactly. The reason is that symplectic integration with a finite step size ideally (i.e. without rounding errors) conserves angular momentum exactly. It also conserves energy, but not the energy of the original Hamiltonian H but of a slightly different one, H^h. The difference between H and H^h is $O(h^r)$, where r is the order of the method.[6] This is what Figure 1 shows. Nevertheless, the absence of energy drift is a big advantage of symplectic integration, especially for long trajectories. We have verified it for S4, and conversely for G in some cases (cf. also ref 10), but do not show it to keep the paper short. As we will see below, the limiting error for our problem is not the energy error, which would allow much longer integration times, but the position error, which makes too long trajectories meaningless.

Finally we back-integrated some of the trajectories. This has often been done to assess the accuracy of trajectory calculations. The argument runs as follows: if trajectories of some length can be back-integrated within a certain error, they will also be correct within that error to twice that length in the forward direction. This may be a correct conclusion for integrators which are not time-reversible. For S6 and S4, however, which are time-reversible, we find that trajectories which are completely wrong, i.e., come out with wrong M and wrong reaction channel, are still back-integrated very exactly. So, at least for this class of integrators, back-integratbility is no proof at all for correctness.

B. Nonconserved Quantities. We now turn to the nonconserved quantities M and $\{\mathbf{q}, \mathbf{p}\}$. Remember that M is a measure for the length and complexity of the trajectories. As we discussed before, the consistency of M on halving the step size was taken as a criterion for correctly computed trajectories. In Table 1 we show for the three integrators the percentage of correctly computed trajectories for different step sizes vs the length of trajectories collected into groups of M. The data show again that S6 is better than G and that S4 is worse than both others.

The error Δx of the end points in phase space is measured as the Euclidean distance from the end point of the QP calculation with the smallest step size (full step $2^{-12} \times 10$ fs for S6, $2^{-14} \times 10$ fs for G). This only makes sense for trajectories with the correct number of MEs, to which our statistics is restricted. We show the behavior of S6 and G in Figures 3 and 4. Again, S6 is orders of magnitude better than G, especially at high accuracy. S4 (not shown) is again worse. Note that Δx is the absolute error in our internal units, the relative error is about one-tenth of the plotted numbers. The saturation of the errror at large M is due to the fact that all trajectories remain bounded in all but one coordinate.

C. General Remarks. We close with some general results derived from this study:

(1) The sixth order symplectic integrator of Teloy,[5] called S6 here, is definitely better (with respect to correctness at given computing expense) than all others, which we have now or earlier[16] tested, and it has very good stability. We will use it henceforth for our routine calculations.

(2) In a chaotic dynamical system like our model with Lyapunov exponents of the order of 0.5 per passage through the well (i.e., per ME), the correct computation of trajectories appears to be limited in DP to those with less than about 40 MEs. (This may perhaps change a little if still better integrators are found.) A number of 40 MEs corresponds to about 0.5 ps for a system with a typical well depth of 5 eV, scattering energy of 1.0 eV, and three masses of about 1 u. From our earlier experience we can state that this result will depend very little on the scattering energy, as long as this is less than about one-third of the (absolute value of the) well depth. For higher energies the lifetime of long-lived trajectories decreases fast, and integration becomes easier. For other masses the correspondence between the number of MEs and real time must be scaled with the square root of the average mass. In QP the limit for correct computation is more than 60 MEs, if one is willing to spend the effort. We did not reach this limit of, perhaps, 80 MEs, because we restricted our step size in view of computing time, which for the smallest time steps peaked already at several days for 1000 trajectories on a IBM R6000/59H workstation.

(3) If a calculation involves many thousands of trajectories, and the final results are statistical averages, one may of course argue that the errors of single trajectories will be compensated for in the ensemble. This argument is sometimes based on the "shadow theorem",[24,25] which states that in chaotic dynamics through any sequence of points lying on an approximate trajectory there exists an exact trajectory of the dynamics through these same points. But this theorem is nonconstructive, and it is unclear and, in practice, impossible to check how far

TABLE 1: Percentage of Correctly Computed Trajectories of Length Groups Measured by the Number of Minimum Exchanges, *M* (See Text), as a Function of the Substep Size $2^{-n} \times 10$ fs with $n = 8...14$ for Double and $n = 8...15$ for Quadruple Precision[a]

	DP							QP							
M group	8	9	10	11	12	13	14	8	9	10	11	12	13	14	15
0−9	97	99	99	100	100	100	100	97	99	99	100	100	100	100	100
	99	100	100	100	100	100	100	99	100	100	100	100	100	100	100
	97	99	99	100	100	100	100	97	99	99	100	100	100	100	100
10−19	94	96	98	98	99	100	100	94	96	98	98	99	100	100	100
	97	98	99	100	100	100	100	97	98	99	100	100	100	100	100
	90	95	97	98	99	100	100	90	95	97	98	99	100	100	100
20−29	93	94	96	99	100	100	100	93	94	96	99	100	100	100	100
	90	96	100	100	100	100	100	90	96	100	100	100	100	100	100
	70	86	90	98	99	100	100	70	86	90	98	99	100	100	100
30−39	67	90	98	97	98	97	98	67	90	98	100	100	100	100	100
	57	77	92	97	95	96	95	57	77	92	97	100	100	100	100
	23	46	62	79	90	95	97	23	46	62	79	90	95	99	100
40−49	31	57	83	88	91	85	83	32	57	82	92	96	99	99	100
	20	38	70	81	81	75	77	20	38	71	83	94	93	93	93
	6	8	25	39	62	77	81	6	8	25	39	63	77	88	94
50−59	9	33	69	73	70	70	66	9	32	67	82	95	96	100	100
	6	17	37	59	65	58	57	4	18	37	67	79	85	86	86
	2	2	7	15	35	59	66	2	2	6	15	36	56	72	84
60−69	5	15	37	45	46	42	37	5	17	43	71	88	97	99	100
	5	6	18	37	28	32	30	4	8	17	39	60	75	77	76
	4	5	2	10	19	27	37	5	5	3	10	18	36	55	75
70−79	4	7	26	35	25	21	31	4	8	30	57	73	87	95	100
	5	1	12	20	20	13	14	2	4	10	24	44	51	52	51
	2	0	5	4	8	20	27	2	1	2	6	10	19	35	56
80−89	0	11	13	16	16	18	13	0	11	8	39	63	100	100	100
	0	3	5	13	16	8	8	3	3	8	16	24	42	39	37
	0	0	3	3	8	13	13	3	3	3	3	3	8	21	45

[a] Note that the number of substeps determines the expense. Upper rows, S6; middle rows, G; lower rows, S4. For simplicity, the number of substeps per step has been approximated here as 8, 4, 2 instead of 9, 5, 2 for S6, S4, and G, respectively.

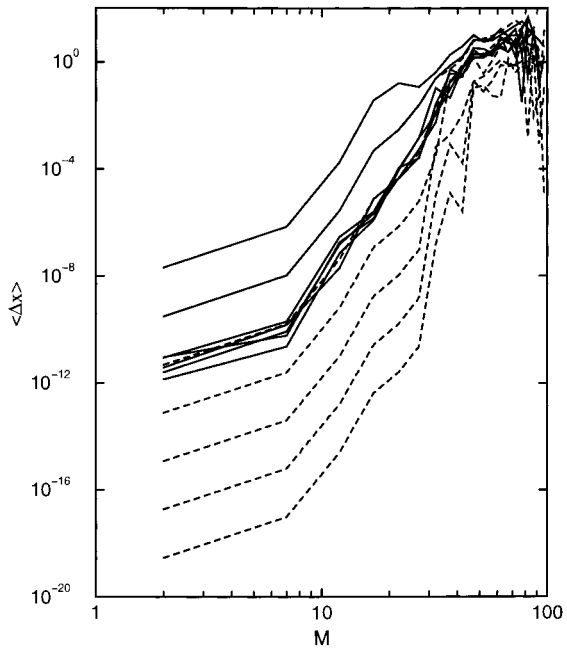

Figure 3. Average error of the end points (measured as the Euclidean distance in phase space from the optimally integrated trajectories) as a function of the number of MEs (approximately proportional to the length of the trajectory) for the sixth order symplectic integrator S6. The *M* numbers are binned into sets of width 5. From top to bottom the curves correspond to substep sizes of $2^{-n} \times 10$ fs with $n = 7...13$, computed in DP (—) or QP (--). The two upmost curves for QP and DP coincide. Relative errors are approximately one-tenth of those plotted.

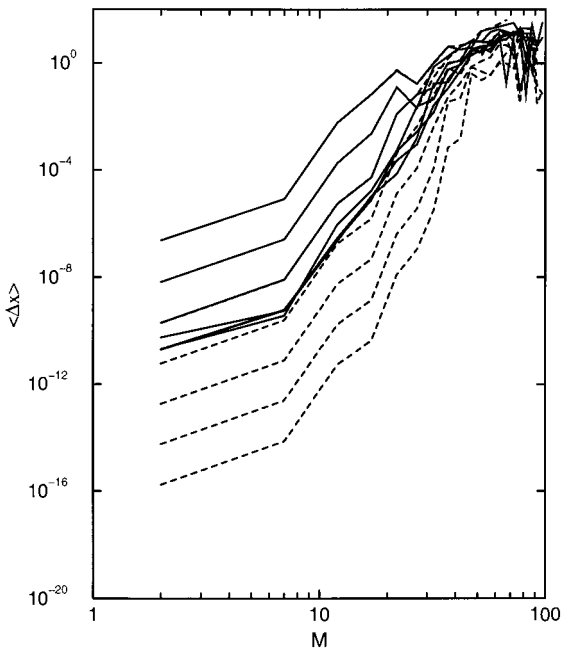

Figure 4. Same as Figure 3 for the Gear integrator G.

the assumptions made in the proof of the theorem hold in a system like ours.

We have tried to shed some light on this "averaging postulate" by looking into a possible dependence on the step size of some ensemble property of our calculations. As a simple example, for which we can get fair statistics, we took the ratio, *r*, of even and odd MEs. For large step sizes ($n = 5$ and 6) we find, indeed, some *r* which are different by about 3σ from the converged (but still fluctuating) limit for small step sizes. Much larger samples are needed to make this test a stringent one.

(4) Finally, one might say that discussing the correctness of single trajectories in molecular dynamics looks a bit "academic". In principle, we should, of course, use quantum mechanics. However, computational problems force us to use classical

mechanics in many cases. But then it is easy to find physical problems for which it is important to know whether a *small number of long trajectories* is correct or not. One such case is the determination of a cross-section for a rarely populated channel. Another is the question of whether the classical unimolecular decay of a microcanonically activated molecule is exponential with a single exponent or not (cf. ref 19). Again, the answer is completely determined by the small numbers of very long-lived trajectories. We may add that these problems are also still far from treatable by quantum calculations.

Concluding, we have verified that a new, sixth order symplectic integrating routine can make the computation of classical trajectories simulating complex scattering or unimolecular decay, much faster than using traditional ones. In addition, this study shows also how careful one must be in assuming trajectories to be correctly computed in chaotic systems.

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