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A FAMILY OF SYMPLECTIC INTEGRATORS: STABILITY, ACCURACY, AND MOLECULAR DYNAMICS APPLICATIONS*

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Abstract. The following integration methods for special second-order ordinary differential equations are studied: leapfrog, implicit midpoint, trapezoid, Störmer–Verlet, and Cowell–Numerov. We show that all are members, or equivalent to members, of a one-parameter family of schemes. Some methods have more than one common form, and we discuss a systematic enumeration of these forms. We also present a stability and accuracy analysis based on the idea of "modified equations" and a proof of symplecticness. It follows that Cowell–Numerov and "LIM2" (a method proposed by Zhang and Schlick) are symplectic. A different interpretation of the values used by these integrators leads to higher accuracy and better energy conservation. Hence, we suggest that the straightforward analysis of energy conservation is misleading.

Key words. leapfrog, Störmer, Verlet, implicit midpoint, trapezoid, Cowell, Numerov, symplectic integrator, molecular dynamics, method of modified equations

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1. Introduction.

Our focus in this paper is a study of a set of methods for systems of special (i.e., see (1) below) second-order ordinary differential equations (ODEs). This set includes the following well-known methods: leapfrog, implicit midpoint, trapezoid, Störmer–Verlet, and Cowell–Numerov. Of special interest to us is the application of such methods to molecular dynamics (MD) of biomolecules. These problems, as well as many other special second-order ODEs, are Hamiltonian systems, and recently there has been much interest in the use of *symplectic integrators* in such contexts. Symplectic methods preserve certain abstract invariants of Hamiltonian systems. Experiments [1, 2] show that symplectic methods give remarkable accuracy for long integration intervals, and it has been shown by Suris [3] that symplectic methods are stable for linear systems for sufficiently small values of the stepsize. Another attractive feature of symplectic integrators is that the error due to a finite timestep can be interpreted as an error in the scalar Hamiltonian function from which the force vector is generated,[1] not merely as an error in the force vector. For further information on symplectic methods for Hamiltonian systems, see [1] and references cited therein.

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[1] To be precise, this is in general not quite true; for a discussion see [1, p. 132].

Our aim here is to unify and simplify the formulation and analysis of several methods for MD in the context of symplecticness. We show that the schemes above are all members, or equivalent to members, of a one-parameter family of methods. This makes implementation unified and comparison facile. Some of these methods have more than one common form, and the various forms are presented here systematically. In the case of the Verlet–leapfrog method, such a dual representation has been discussed in [4, 5].

Also presented are a stability analysis, an accuracy analysis based on the idea of "modified equations," and a proof of symplecticness. A particular by-product of this result is a demonstration that both the fourth-order Cowell–Numerov and the method LIM2 of Zhang and Schlick [6] are symplectic. The values used by all these integrators can be interpreted in a slightly different and more favorable way through trajectory transformations, leading to higher accuracy and better energy conservation. As a consequence, we suggest that the straightforward analysis of energy conservation is misleading. That is, energy conservation alone can suggest, for example, that the implicit midpoint method is more accurate than the Verlet method, but in fact Verlet is twice as accurate. Numerical experiments on a model of butane support the results of the asymptotic analysis for the moderately low accuracies used for MD.

The idea of interpreting numerical values in a more favorable way is similar to an idea of Butcher [7] for increasing the order of Runge–Kutta methods. In the more specific context of symplectic integration this idea appears in a lively paper [8] motivated by solar system dynamics. Also, earlier papers [9, 10] essentially have the same idea. One difference between the work in [8] and our approach is that they use Hamiltonian flows whereas we use generating functions to construct the transformation between what they call "mapping variables" and "real variables." Our numerical results for molecule dynamics give further evidence of their assertion that one can "relate the mapping variables to the real variables and consequently remove the spurious oscillations" to a large degree.

In the family of methods we consider, all are implicit except for Verlet. Thus, it is reasonable to question the practicality of the implicit method for biomolecular MD. Various techniques for accelerating the solution process of the resulting nonlinear system [11, 12] have been devised to make computational cost manageable, even competitive at moderate timesteps. Moreover, implicit methods might be viewed as starting points for deriving cheaper methods that have nearly as good stability and accuracy properties. Thus, further development of implicit schemes for such large-scale problems is warranted.

We consider the system of ODEs

$$M\frac{d^2x}{dt^2} = F(x), \tag{1}$$

where x is the collective position vector, M is a diagonal matrix of masses, and F is the collective force vector. We now describe the Störmer–Verlet, leapfrog, Cowell–Numerov, LIM2, implicit midpoint, and trapezoid schemes. The discretization known as the second-order Störmer method is given by

$$\frac{1}{\Delta t^2}M(X^{n+1} - 2X^n + X^{n-1}) = F(X^n), \tag{2}$$

where Δt is the timestep, and X^n denotes the difference approximation to x at time $n\Delta t$. This scheme was derived from a truncation of the higher-order method used by

Störmer [13] to integrate trajectories of electrons in the aurora borealis. Toxvaerd [14] states that "the first known published appearance [of this method] is due to Joseph Delambre (1791) [15, 16]." This method was proposed as an integrator for MD by Verlet [17] together with the formula

$$V^n = \frac{1}{2\Delta t}(X^{n+1} - X^{n-1}) \tag{3}$$

for calculating the velocity $v = \frac{dx}{dt}$. It is known [18, p. 80] that this combination is equivalent to the leapfrog method, defined as

$$V^{n+1/2} = V^{n-1/2} + \Delta t M^{-1} F(X^n), \tag{4}$$

$$X^{n+1} = X^n + \Delta t V^{n+1/2}. \tag{5}$$

The implicit discretization scheme with a different right-hand side than in (2),

$$\frac{1}{\Delta t^2} M(X^{n+1} - 2X^n + X^{n-1}) = \frac{1}{12}F(X^{n-1}) + \frac{5}{6}F(X^n) + \frac{1}{12}F(X^{n+1}), \tag{6}$$

is often known as "Cowell's method." It was used by Cowell and Crommelin [19] to predict the return of Halley's comet in 1909. In the context of two-point boundary value problems it is known as "Numerov's method." The coefficients of the forces are chosen to yield fourth-order accuracy.

The method "LIM2" of Zhang and Schlick [6] is defined by

$$\frac{1}{\Delta t^2} M(X^{n+1} - 2X^n + X^{n-1}) = F\left(\frac{1}{2}(X^{n+1} + X^{n-1})\right). \tag{7}$$

This method was proposed in a paper comparing performance of several implicit integrators for the Langevin equation, including implicit-Euler and implicit midpoint. Both LIM2 and the midpoint method were found to be superior to the first-order implicit schemes because they possess no intrinsic (numerical) damping on the basis of linear analysis. However, resonance problems have been recently reported and analyzed with the implicit midpoint [20]. The implicit midpoint method is given by the pair

$$\frac{1}{\Delta t}(X^{n+1} - X^n) = \frac{1}{2}(V^{n+1} + V^n), \quad \frac{1}{\Delta t} M(V^{n+1} - V^n) = F\left(\frac{1}{2}(X^{n+1} + X^n)\right), \tag{8}$$

and the trapezoid method is similar, using only a different force approximation:

$$\frac{1}{\Delta t}(X^{n+1} - X^n) = \frac{1}{2}(V^{n+1} + V^n), \quad \frac{1}{\Delta t} M(V^{n+1} - V^n) = \frac{1}{2}\left(F(X^{n+1}) + F(X^n)\right). \tag{9}$$

These two equations are known to be equivalent [21].

As we will show, all methods above are members of the one-parameter family of symplectic methods presented in this paper. For leapfrog–Störmer–Verlet $\alpha = 0$, for Numerov–Cowell $\alpha = \frac{1}{12}$, for implicit midpoint–trapezoid $\alpha = \frac{1}{4}$, and for LIM2 method $\alpha = \frac{1}{2}$. Equivalence here means that by some operation (applied to values that are only local in time) we can transform values obtained by one method so that they satisfy another. For example, if the values X^n, V^n are obtained by the trapezoid method, the transformation

$$\hat{X}^n = X^n - \frac{\Delta t}{2} V^n, \quad \hat{V}^n = V^n - \frac{\Delta t}{2} M^{-1} F(X^n)$$

gives values $\hat{X}^n$, $\hat{V}^n$ that would be obtained by the implicit midpoint method. (This transformation is obtained by observing that one step of the trapezoid method is equivalent to a step of forward Euler with timestep $\frac{\Delta t}{2}$ followed by a step of backward Euler with timestep $\frac{\Delta t}{2}$. Similarly, implicit midpoint corresponds to backward Euler followed by forward Euler.)

2. Formulation. We now describe the basic form of our family of integrators and associate specific values of the parameter α with different integrators. At the beginning of step $(n+1)$, we assume that we know the collective position and velocity vectors X^n and V^n as well as the collective force vector F^n. In particular, F^n has been obtained by solving the nonlinear system

$$F^n = F(X^n + \alpha \Delta t^2 M^{-1} F^n), \tag{10}$$

where α is the parameter defining each method within our family of schemes. Note that (10) is an implicit equation for F^n for $\alpha \neq 0$. Below we describe several forms (e.g., 1E, 2M, 1$\bar{\text{E}}$) for defining one integration step, that is, updating formulas for position, velocity, and force. Suffixes E and M distinguish between formulas that involve evaluation (to derive the implicitly defined force) at the endpoints and midpoints, respectively. Prefixes 1 and 2 are taken from standard terminology in the numerical solution of ODEs: "1" for a one-step scheme that involves both position and velocity, "2" for a two-step scheme that only depends on position; in the latter case, the velocity can be computed by various definitions (e.g., (3)), and this choice does not affect the positional trajectory. Finally, we use bar notation in the propagation title to denote a scheme that uses $\bar{X}^n \equiv X^n + \alpha \Delta t^2 F^n$ instead of X^n (this will become clear below). With these notations at hand, we now define propagation forms 1E, 1M, 1$\bar{\text{E}}$, 2E, 2M, and 2$\bar{\text{E}}$. We show that 1E, 1M, 1$\bar{\text{E}}$ can be related to the Verlet (and related leapfrog), implicit midpoint, and trapezoid schemes. Forms 2E and 2$\bar{\text{E}}$ can be related to the LIM2 and Cowell methods.

Form 1E.

$$\begin{aligned} V^{n+1/2} &= V^n + \frac{\Delta t}{2} M^{-1} F^n, \\ X^{n+1} &= X^n + \Delta t V^{n+1/2}, \\ F^{n+1} &= F(X^{n+1} + \alpha \Delta t^2 M^{-1} F^{n+1}), \\ V^{n+1} &= V^{n+1/2} + \frac{\Delta t}{2} M^{-1} F^{n+1}. \end{aligned} \tag{11}$$

This propagation is classified as "E" because the force calculation occurs at the end of the time subinterval (i.e., F^{n+1}). Within this definition, there are several ways to write the MD equations. If we eliminate the intermediate value $V^{n+1/2}$, we obtain

$$V^{n+1} = V^n + \frac{\Delta t}{2} M^{-1} (F^n + F^{n+1}) \tag{12}$$

for the velocity. We can also offer a one-parameter family of formulas for the position, of which the most interesting ones are

$$X^{n+1} = X^n + \Delta t V^n + \frac{\Delta t^2}{2} M^{-1} F^n \tag{13}$$

and

$$X^{n+1} = X^n + \frac{\Delta t}{2}(V^{n+1} + V^n) - \frac{\Delta t^2}{4} M^{-1}(F^{n+1} - F^n). \tag{14}$$

For $\alpha = 0$, (12) and (13) coincide with the known "velocity Verlet" scheme [18, p. 81]. The related leapfrog method is obtained by replacing computations of V^n for integer values of n by computations of the velocity at the midpoint of the interval only, using

$$V^{n+1/2} = V^{n-1/2} + \Delta t M^{-1} F^n. \tag{15}$$

Instead of omitting velocities at integral n, we can also define additional positions $X^{n+1/2} = X^n + \frac{\Delta t}{2} V^{n+1/2}$.

If we relabel $X^{n-1/2}$ and $V^{n-1/2}$ as X^n and V^n, respectively, we get the midpoint form of our propagation (not to be confused with the midpoint method).

Form 1M.

$$\begin{aligned} X^{n+1/2} &= X^n + \frac{\Delta t}{2} V^n, \\ F^{n+1/2} &= F(X^{n+1/2} + \alpha \Delta t^2 M^{-1} F^{n+1/2}), \\ V^{n+1} &= V^n + \Delta t M^{-1} F^{n+1/2}, \\ X^{n+1} &= X^{n+1/2} + \frac{\Delta t}{2} V^{n+1}. \end{aligned} \tag{16}$$

If we eliminate the intermediate values $X^{n+1/2}$ and $F^{n+1/2}$, we have in analogy to (12) and (13) above

$$X^{n+1} = X^n + \frac{\Delta t}{2}(V^n + V^{n+1}) \tag{17}$$

for the position and a (one-parameter) family of formulas for the velocity. The most interesting representatives of this family are

$$V^{n+1} = V^n + \Delta t M^{-1} F\left(X^n + \frac{\Delta t}{2} V^n + \alpha \Delta t (V^{n+1} - V^n)\right) \tag{18}$$

and

$$V^{n+1} = V^n + \Delta t M^{-1} F\left(\frac{1}{2}(X^{n+1} + X^n) + \left(\alpha - \frac{1}{4}\right) \Delta t (V^{n+1} - V^n)\right). \tag{19}$$

Equation (17) and (19) with $\alpha = \frac{1}{4}$ coincide with the usual formulation of the implicit midpoint method.

If we use $\bar{X}^n$ rather than X^n as our variable, we have another variant.

Form 1$\overline{\text{E}}$.

$$\bar{X}^{n+1} = \bar{X}^n + \frac{\Delta t}{2}(V^{n+1} + V^n) + \left(\alpha - \frac{1}{4}\right) \Delta t^2 M^{-1} (F^{n+1} - F^n), \tag{20}$$

$$V^{n+1} = V^n + \frac{\Delta t}{2} M^{-1} (F^n + F^{n+1}). \tag{21}$$

In this formulation the method is technically not symplectic for $\alpha \neq 0$. With $\alpha = \frac{1}{4}$, we recover the trapezoidal rule.

If we eliminate V^n from form 1E, we obtain $\Delta t^{-2} M^{-1}(X^{n+1} - 2X^n + X^{n-1}) = F^n$ where F^n is defined in (10). Using the first relation to substitute for F^n in the right-hand side of (10), we get our next form.

Form 2E.

$$\frac{1}{\Delta t^2} M (X^{n+1} - 2X^n + X^{n-1}) = F(\alpha X^{n-1} + (1 - 2\alpha) X^n + \alpha X^{n+1}). \tag{22}$$

The velocities can be recovered by setting

$$V^n = \frac{1}{2\Delta t}(X^{n+1} - X^{n-1}). \tag{23}$$

For $\alpha = \frac{1}{2}$ this is the form given by [6] for the method LIM2.

If we eliminate V^n from 1M, we have form 2M.

Form 2M.

$$\frac{1}{\Delta t^2} M(X^{n+1} - 2X^n + X^{n-1}) = \frac{1}{2}F^{n-1/2} + \frac{1}{2}F^{n+1/2}, \tag{24}$$

where

$$F^{n+1/2} = F\left(\frac{1}{2}(X^n + X^{n+1}) + (\alpha - \frac{1}{4})\Delta t^2 M^{-1}F^{n+1/2}\right). \tag{25}$$

The velocity is obtained from

$$V^n = \frac{1}{2\Delta t}(X^{n+1} - X^{n-1}) - \frac{\Delta t}{4}M^{-1}(F^{n+1/2} - F^{n-1/2}). \tag{26}$$

We know of no use of this form in the literature.

If we eliminate V^n from $1\overline{\text{E}}$, we have our final variant.

Form $2\overline{\text{E}}$.

$$\frac{1}{\Delta t^2} M(\bar{X}^{n+1} - 2\bar{X}^n + \bar{X}^{n-1}) = \alpha F^{n-1} + (1 - 2\alpha)F^n + \alpha F^{n+1}, \tag{27}$$

with the velocity formula:

$$V^n = \frac{1}{2\Delta t}(\bar{X}^{n+1} - \bar{X}^{n-1}) - \frac{\alpha\Delta t}{2}M^{-1}(F^{n+1} - F^{n-1}). \tag{28}$$

With $\alpha = \frac{1}{12}$, this form coincides with the Cowell method. The formal order of accuracy (four) is such only in this form and only for $\bar{X}^n$. Some favor this form [14] because it is in some sense canonical: it involves only those "special" values at which the force is evaluated, all other values being regarded as ad hoc combinations of these.

Although six forms have been offered above, we favor form 1E for the following reasons:

1. This form has good round-off error compared with forms 2E, 2M, $2\overline{\text{E}}$ since cancellation is avoided [22, p. 472]. Because of the exponential growth of errors [18], this aspect cannot be ignored, especially with the use of single precision.
2. Form 1E generalizes efficiently to multiple timestepping [23, 24, 25] compared with form 1M.
3. Form 1E is symplectic unlike form $1\overline{\text{E}}$, which instead of using X^n uses the more natural values

   $$\bar{X}^n := X^n + \alpha\Delta t^2 M^{-1}F^n, \tag{29}$$

   which are the points at which F is evaluated. Nonetheless, it can be shown that $1\bar{E}$ is equivalent to a symplectic method. Still, we prefer to use a symplectic form, since this helps design method variants that retain symplecticness; we also would expect that values computed in this form *might* be better behaved.

Below and in the next section we restrict ourselves to conservative forces for which $F(x) = -E_x(x)$ for some potential energy function $E(x)$ where $E_x(x)$ is the gradient of the potential energy function. In this case the Jacobian matrix for the force vector is symmetric. This property can be exploited, as shown in [6], to express the nonlinear systems of equations as an optimization problem. If we regard $f = F^n$ as our variable of unknowns, the problem becomes finding a minimum of

$$\frac{1}{2}\Delta t^2 f^{\mathrm{T}} M^{-1} f + \alpha^{-1} E(X^{n+1} + \alpha \Delta t^2 M^{-1} f). \tag{30}$$

For $\alpha = 0$ (explicit method), the second term becomes $\Delta t^2 E_x(X^{n+1})^{\mathrm{T}} M^{-1} f$. If instead we use $X = X^{n+1} + \alpha \Delta t^2 M^{-1} f$ as the variable, the minimization problem for the "dynamics function" $\Phi(X)$ is formed, where

$$\Phi(X) = \frac{1}{2}\Delta t^{-2}(X - X^{n+1})^{\mathrm{T}} M (X - X^{n+1}) + \alpha E(X). \tag{31}$$

Clearly, many solutions that minimize Φ exist [26]. However, we want a nearby solution in some sense. For example, we may seek the solution that will be obtained by analytical continuation as α varies from 0 to its desired value. This solution will be well defined as long as the Hessian of the dynamics function Φ remains positive definite. When positive definiteness does not hold, we may consider the timestep to be too large.

3. Accuracy. We now analyze accuracy by the "method of modified equations," introduced in computational fluid dynamics [27, 1] to interpret the effect of discretization error as a change in the mathematical equations. The idea is based on the assumption that the numerical values (X^n, V^n) are *exact* values of functions $(X(t), V(t))$ that satisfy differential equations with slightly different right-hand sides, which are assumed to possess asymptotic expansions in powers of Δt. We, in fact, use $P = MV$ (momenta) instead of V as variables so that our given system is Hamiltonian:

$$\frac{dx}{dt} = H_p(x,p), \qquad \frac{dp}{dt} = -H_x(x,p), \tag{32}$$

where $H(x,p) = \frac{1}{2}p^{\mathrm{T}} M^{-1} p + E(x)$.

After a somewhat lengthy calculation, described in the subsection that follows, we get a Hamiltonian system, at least up to $O(\Delta t^4)$,

$$\begin{aligned} \frac{dX}{dt} &= \tilde{H}_p(X,P) + O(\Delta t^4), \\ \frac{dP}{dt} &= -\tilde{H}_x(X,P) + O(\Delta t^4) \end{aligned}$$

with

$$\begin{aligned} \tilde{H}(X,P) &= \frac{1}{2}P^{\mathrm{T}} M^{-1} P + E(X) \\ &\quad + \Delta t^2 \left(\frac{1}{12}(M^{-1}P)^{\mathrm{T}} E_{xx}(X) M^{-1} P - \left(\frac{1}{24} + \frac{1}{2}\alpha \right) E_x(X)^{\mathrm{T}} M^{-1} E_x(X) \right) \end{aligned} \tag{33}$$

where $E_{xx}(X)$ is the Hessian of the potential energy function. One can carry the expansion as far as one likes (although it may not converge if carried to infinity).

A similar result holds for the M form of the method. Again, after some calculations, given in the subsection that follows, we obtain a Hamiltonian system, at least up to $O(\Delta t^4)$, with

$$\tilde{H}(X,P) = \frac{1}{2}P^{\mathrm{T}}M^{-1}P + E(X) + \Delta t^2\left(-\frac{1}{24}(M^{-1}P)^{\mathrm{T}}E_{xx}(X)M^{-1}P + \left(\frac{1}{12}-\frac{1}{2}\alpha\right)E_x(X)^{\mathrm{T}}M^{-1}E_x(X)\right). \tag{34}$$

3.1. Calculation of modified Hamiltonians. We begin with the E form. First note that

$$F^n = -E_x(X^n) + \alpha\Delta t^2 E_{xx}(X^n)M^{-1}E_x(X^n) + O(\Delta t^4).$$

Expanding (14) and (12) in a Taylor series about $t = t_n + \frac{1}{2}\Delta t$, we get

$$\begin{aligned}
\Delta t\frac{dX}{dt} + \frac{\Delta t^3}{24}\frac{d^3X}{dt^3} &= \Delta t M^{-1}P + \frac{\Delta t^3}{8}M^{-1}\frac{d^2P}{dt^2} + \frac{\Delta t^3}{4}\frac{d[M^{-1}E_x(X)]}{dt} + O(\Delta t^5),\\
\Delta t\frac{dP}{dt} + \frac{\Delta t^3}{24}\frac{d^3P}{dt^3} &= -\Delta t E_x(X) - \frac{\Delta t^3}{8}\frac{d^2}{dt^2}[E_x(X)]\\
&\quad +\alpha\Delta t^3 E_{xx}(X)M^{-1}E_x(X) + O(\Delta t^5),
\end{aligned}$$

where $X = X(t_n + \frac{\Delta t}{2})$, $P = P(t_n + \frac{\Delta t}{2})$. Hence

$$\begin{aligned}
\frac{dX}{dt} &= M^{-1}P + \Delta t^2\left(\frac{1}{8}M^{-1}\frac{d^2P}{dt^2} + \frac{1}{4}M^{-1}E_{xx}(X)\frac{dX}{dt} - \frac{1}{24}\frac{d^3X}{dt^3}\right) + O(\Delta t^4),\\
\frac{dP}{dt} &= -E_x(X) + \Delta t^2\left(-\frac{1}{8}E_{xxx}(X)\left(\frac{dX}{dt},\frac{dX}{dt}\right) - \frac{1}{8}E_{xx}(X)\frac{d^2X}{dt^2}\right.\\
&\quad \left. +\alpha E_{xx}(X)M^{-1}E_x(X) - \frac{1}{24}\frac{d^3P}{dt^3}\right) + O(\Delta t^4).
\end{aligned}$$

The double summation involved in $E_{xxx}(X)$ is indicated with multilinear notation. By successive substitution we get

$$\begin{aligned}
\frac{dX}{dt} &= M^{-1}P + \Delta t^2\left(\frac{1}{6}M^{-1}E_{xx}(X)M^{-1}P\right) + O(\Delta t^4),\\
\frac{dP}{dt} &= -E_x(X) + \Delta t^2\left(-\frac{1}{12}E_{xxx}(X)M^{-1}PM^{-1}P\right.\\
&\quad \left. + \left(\frac{1}{12}+\alpha\right)E_{xx}(X)M^{-1}E_x(X)\right) + O(\Delta t^4);
\end{aligned}$$

hence (33) follows.

We obtain the result for the M form as a consequence of the result for the E form. We begin by getting the transformation that links the two forms. For this we need to relate values X^n, P^n to values $X^{n-1/2}$, $P^{n-1/2}$; making use of the various definitions, we get

$$\begin{aligned}
X^n &= X^{n-1/2} + \frac{\Delta t}{2}M^{-1}P^{n-1/2},\\
P^n &= P^{n-1/2} + \frac{\Delta t}{2}F\left(X^{n-1/2} + \left(\frac{1}{2}-2\alpha\right)\Delta t M^{-1}P^{n-1/2} + 2\alpha\Delta t M^{-1}P^n\right),
\end{aligned}$$

which is implicit in P^n. If we let hat superscripts denote values for the 1M form, we have

$$X = \hat{X} + \frac{\Delta t}{2} M^{-1} \hat{P},$$
$$P = \hat{P} + \frac{\Delta t}{2} F\left(\hat{X} + \left(\frac{1}{2} - 2\alpha\right) \Delta t M^{-1} \hat{P} + 2\alpha \Delta t M^{-1} P\right).$$

To make the transformation explicit, we expand it in powers of Δt:

$$P = \hat{P} - \frac{1}{2}\Delta t E_x(\hat{X}) - \frac{1}{4}\Delta t^2 E_{xx}(\hat{X}) M^{-1}\hat{P} + \frac{\alpha}{2}\Delta t^3 E_{xx}(\hat{X}) M^{-1} E_x(\hat{X}) - \frac{1}{16}\Delta t^3 E_{xxx}(\hat{X})(M^{-1}\hat{P}, M^{-1}\hat{P}) + O(\Delta t^4).$$

Finally, we substitute this into (33), obtaining

$$\tilde{H}(X(\hat{X},\hat{P}), P(\hat{X},\hat{P})) = \frac{1}{2}\hat{P}^{\mathrm{T}} M^{-1}\hat{P} + E(\hat{X}) + \Delta t^2 \left(-\frac{1}{24}(M^{-1}\hat{P})^{\mathrm{T}} E_{xx}(\hat{X}) M^{-1}\hat{P} + \left(\frac{1}{12} - \frac{1}{2}\alpha\right) E_x(\hat{X})^{\mathrm{T}} M^{-1} E_x(\hat{X})\right). \tag{35}$$

4. Stability. Stability analysis performed for the harmonic oscillator case, as in [6], gives insight into the dynamic behavior of simple systems. That is, we examine solution behavior for the linear-force case

$$\frac{d^2x}{dt^2} = -\omega^2 x, \tag{36}$$

where ω is the natural angular velocity of the oscillator. However, nonlinearities also play an important role; for example, investigations [28] show that the implicit midpoint rule has to obey timestep restrictions not present for linear problems. The long-time behavior is an entirely different problem [29].

For our stability analysis, it is more convenient to switch to the midpoint form. We separate this form into half steps to obtain

$$\begin{aligned} X^{n+1/2} &= X^n + \frac{\Delta t}{2} V^n, \\ V^{n+1/2} &= V^n + \frac{\Delta t}{2} M^{-1} F^{n+1/2}, \\ V^{n+1} &= V^{n+1/2} + \frac{\Delta t}{2} M^{-1} F^{n+1/2}, \\ X^{n+1} &= X^{n+1/2} + \frac{\Delta t}{2} V^{n+1}, \end{aligned} \tag{37}$$

where

$$F^{n+1/2} = F(X^{n+1/2} + \alpha \Delta t^2 M^{-1} F^{n+1/2}). \tag{38}$$

Denoting the force $F(X) = -\omega^2 X$, we have

$$F^{n+1/2} = -\phi\omega^2 X^{n+1/2}, \tag{39}$$

where

$$\phi := (1 + \alpha(\omega\Delta t)^2)^{-1}. \tag{40}$$

Using matrix multiplication to represent each of the four stages, we obtain

$$\begin{bmatrix} \omega X^{n+1} \\ V^{n+1} \end{bmatrix} = S \begin{bmatrix} \omega X^{n} \\ V^{n} \end{bmatrix}, \tag{41}$$

where

$$\begin{aligned} S &= \begin{bmatrix} 1 & \frac{1}{2}\omega\Delta t \\ 0 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ -\frac{1}{2}\phi\omega\Delta t & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 \\ -\frac{1}{2}\phi\omega\Delta t & 1 \end{bmatrix} \begin{bmatrix} 1 & \frac{1}{2}\omega\Delta t \\ 0 & 1 \end{bmatrix} \\ &= \begin{bmatrix} 1-\frac{1}{4}\phi(\omega\Delta t)^2 & \frac{1}{2}\omega\Delta t \\ -\frac{1}{2}\phi\omega\Delta t & 1 \end{bmatrix} \begin{bmatrix} 1 & \frac{1}{2}\omega\Delta t \\ -\frac{1}{2}\phi\omega\Delta t & 1-\frac{1}{4}\phi(\omega\Delta t)^2 \end{bmatrix} \\ &= \begin{bmatrix} 1-\frac{1}{2}\phi(\omega\Delta t)^2 & \omega\Delta t(1-\frac{1}{4}\phi(\omega\Delta t)^2) \\ -\phi\omega\Delta t & 1-\frac{1}{2}\phi(\omega\Delta t)^2 \end{bmatrix}. \end{aligned} \tag{42}$$

We obtain nearly the same result for the endpoint form if we use $\bar{X}$ instead of X.

It can be shown that the matrix S is power bounded if and only if $\phi(\omega\Delta t)^2 < 4$. If $\alpha \geq \frac{1}{4}$, this is satisfied for all $\omega\Delta t$, and the method is unconditionally stable. If $\alpha < \frac{1}{4}$, this boundedness is satisfied for $\omega\Delta t < 2(1-4\alpha)^{-1/2}$. Thus, we know that the leapfrog–Störmer–Verlet method ($\alpha = 0$) is stable if and only if $\omega\Delta t < 2$.

If we assume that

$$\phi(\omega\Delta t)^2 < 4, \tag{43}$$

the matrix S has eigenvalues $e^{\pm i\theta}$ where

$$\begin{aligned} \theta &= 2\arcsin\left(\sqrt{\phi}\,\frac{\omega\Delta t}{2}\right) \\ &= \omega\Delta t + \left(\frac{1}{24} - \frac{\alpha}{2}\right)(\omega\Delta t)^3 + O((\omega\Delta t)^5). \end{aligned} \tag{44}$$

Thus, θ is method and timestep dependent. For $\alpha = \frac{1}{4}$, this angular expression simplifies to $\theta = 2\arctan\frac{\omega\Delta t}{2}$. The matrix S can be written as

$$S = DQD^{-1} \tag{45}$$

where

$$Q = \begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix} \tag{46}$$

and

$$D = \operatorname{diag}\left[1, \left(1 + \left(\alpha - \frac{1}{4}\right)(\omega\Delta t)^2\right)^{-1/2}\right] = \operatorname{diag}\left[1, 1 + (1-4\alpha)\tan^2\frac{\theta}{2}\right]. \tag{47}$$

The matrix Q represents a rotation of $-\theta$ radians in phase space. Note that $D_{22} > 0$. To study the propagation behavior in time, we examine

$$S^n = DQ^nD^{-1} \tag{48}$$

where

$$Q^n = \begin{bmatrix} \cos n\theta & \sin n\theta \\ -\sin n\theta & \cos n\theta \end{bmatrix}.$$

We can find a closed form expression for the modified Hamiltonian in this case. Expressing our closed form numerical solution in terms of the variable t, we get the evolution formula for positions and velocities:

$$\begin{bmatrix} \omega X(t) \\ V(t) \end{bmatrix} = DQ^{t/\Delta t}D^{-1} \begin{bmatrix} \omega X(0) \\ V(0) \end{bmatrix}. \tag{49}$$

To get the differential equation satisfied by this general solution of an initial value problem, we differentiate with respect to t,

$$\frac{d}{dt}\begin{bmatrix} \omega X(t) \\ V(t) \end{bmatrix} = D\frac{\theta}{\Delta t}\begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} Q^{t/\Delta t}D^{-1}\begin{bmatrix} \omega X(0) \\ V(0) \end{bmatrix}$$

and eliminate the initial values from these two last equations:

$$\frac{d}{dt}\begin{bmatrix} \omega X(t) \\ V(t) \end{bmatrix} = \frac{\theta}{\Delta t}D\begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} D^{-1}\begin{bmatrix} \omega X(t) \\ V(t) \end{bmatrix}.$$

This simplifies to

$$\frac{d}{dt}\begin{bmatrix} X(t) \\ V(t) \end{bmatrix} = \frac{\theta}{\omega\Delta t}D_{22}\begin{bmatrix} 0 & D_{22}^{-2} \\ -\omega^2 & 0 \end{bmatrix}\begin{bmatrix} X(t) \\ V(t) \end{bmatrix},$$

which with $P = V$ is a Hamiltonian system with Hamiltonian

$$\frac{\theta}{\omega\Delta t}D_{22}\left(\frac{1}{2}\omega^2X^2 + \frac{1}{2}D_{22}^{-2}P^2\right).$$

Energy is conserved exactly if we use $D_{22}^{-1}V^n$ for the velocity.[2]

The numerical integrator is using θ given in (44) as an approximation to the rotation angle $\omega\Delta t$. In Figure 1, we show the effective rotation versus the desired rotation for $\alpha = 0, \frac{1}{12}, \frac{1}{4} - \frac{1}{\pi^2}, \frac{1}{4}, \frac{1}{2}$. The straight line $\theta = \omega\Delta t$ that represents the desired rotation is shown for reference. The errors in the phase angle are also displayed in Figure 1, $\theta - \omega\Delta t$. Note that the explicit method ($\alpha = 0$) displays rapid divergence from the target value as Δt is increased. The value $\alpha = \frac{1}{12}$ (Cowell method) gives the best fit for smaller values of $\omega\Delta t$. The value $\alpha = \frac{1}{4} - \frac{1}{\pi^2}$ (curve c) gives the best fit over the longest achievable range, namely $[0, \pi]$ (see next paragraph).

If $\alpha < \frac{1}{4}$ (e.g., Verlet, Numerov–Cowell), then as $\omega\Delta t$ ranges from 0 to $2(1 - 4\alpha)^{-1/2}$, the effective rotation angle varies from 0 to π. If $\alpha \geq \frac{1}{4}$ (e.g., midpoint, LIM2), then, as $\omega\Delta t$ ranges from 0 to $+\infty$, the effective rotation angle ranges from 0 to $2\arcsin(1/(2\sqrt{\alpha}))$. This upper bound on the rotation angle equals π for $\alpha = \frac{1}{4}$ (e.g., midpoint) but decreases for larger values of α; e.g., it is $\frac{\pi}{2}$ for $\alpha = \frac{1}{2}$ (e.g., LIM2). Since $\theta = \pi$ is the largest attainable rotation angle, we might ask for the best uniform approximation of the desired rotation angle $\omega\Delta t$ by the effective rotation angle θ for

[2]For $\alpha = 0$, the associated value $D_{22}^{-1} = (1 - \frac{1}{4}(\omega\Delta t)^2)^{1/2}$ can be compared with the value $(1 - \frac{1}{4}(\omega\Delta t)^2)^{-1/2}$ obtained in [14, eqn. (14)] for the velocity scale factor in the *E form* of the Verlet method.

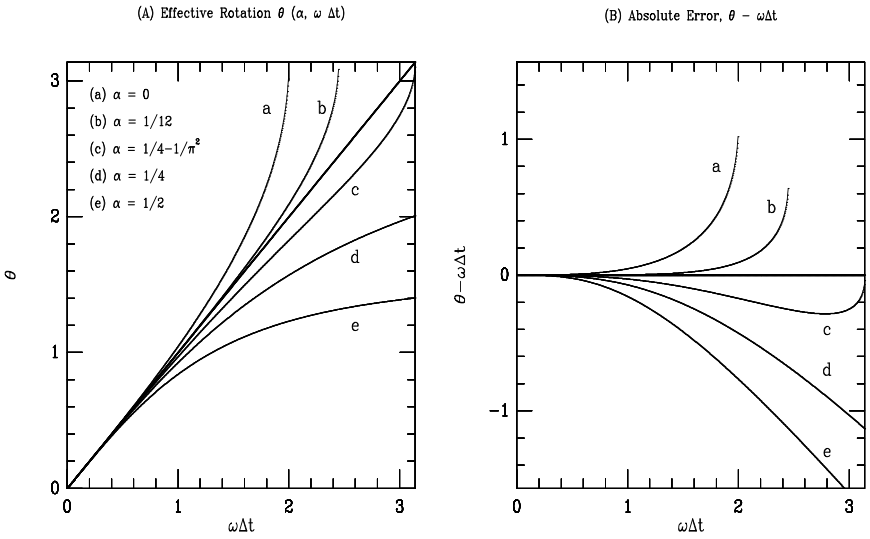

FIG. 1. *The effective phase space rotation and associated error of various integrators for the dynamics of a harmonic oscillator. In* (a)*, the effective rotation* $\theta = 2\sin^{-1}[\omega\Delta t/(2(1+\alpha\omega^2\Delta t^2)^{1/2})]$ *(in radians) is plotted against* $\omega\Delta t$*, and in* (b) $\theta - \omega\Delta t$ *is also shown for various values of* α *that define the integration scheme. The thick solid line corresponds to* $\theta = \omega\Delta t$*.*

$0 \le \omega\Delta t \le \pi$. It is reasonable to require θ to be well defined on this interval and thus $2(1-4\alpha)^{1/2} \ge \pi$ or, equivalently, $\alpha \ge \frac{1}{4} - \frac{1}{\pi^2}$. This gives an approximation for $\theta \approx \omega\Delta t$ whose graph is strictly below the true value; greater values of α cause the graph to drop still further. Hence the best approximation is given by

$$\alpha = \frac{1}{4} - \frac{1}{\pi^2}, \tag{50}$$

which is displayed in curve c.

It should be mentioned that one could also seek the best approximation over a shorter interval and/or the best relative rather than absolute error (since higher frequencies have smaller amplitudes). Alternatively, an α may be sought on the basis of energy conservation. In this case, α can be obtained in tandem with the unknown $3N$-component collective force vector by solving a slightly augmented system of nonlinear equations

$$F^{n+1/2} = F(q^{n+1/2} + \alpha M^{-1}\Delta t^2 F^{n+1/2}),$$

where α is chosen to yield the same energy for step n and $n+1$. In solving this system it might be helpful to know that $\alpha = \frac{1}{4}$ is the solution in the linear case. However, this method entails the cost of evaluating an additional force at the midpoint of the interval, as well as an energy evaluation at the endpoint. Furthermore, this method is not symplectic. We can compare this method with Simo's energy-momentum method [30], which uses

$$F^{n+1/2} = \sigma F\left(q^{n+1/2} + \frac{1}{4}\Delta t^2 F^{n+1/2}\right),$$

where σ is chosen to exactly conserve energy. The advantage of the new method is that it is much more specific to the high frequency modes for a linear problem via a factor $1/(1+\alpha(\omega\Delta t)^2)$ rather than σ.

5. Symplecticness. A simple algebraic test can be formulated to determine whether a numerical integrator is symplectic. A thorough treatment of this concept can be obtained from [1]. Specifically, a transformation between phase spaces $(x, p) \mapsto (X, P)$ is *symplectic* if and only if its Jacobian matrix satisfies the following condition:

$$\begin{bmatrix} \frac{\partial X}{\partial x} & \frac{\partial X}{\partial p} \\ \frac{\partial P}{\partial x} & \frac{\partial P}{\partial p} \end{bmatrix}^{\mathrm{T}} \begin{bmatrix} 0 & I \\ -I & 0 \end{bmatrix} \begin{bmatrix} \frac{\partial X}{\partial x} & \frac{\partial X}{\partial p} \\ \frac{\partial P}{\partial x} & \frac{\partial P}{\partial p} \end{bmatrix} = \begin{bmatrix} 0 & I \\ -I & 0 \end{bmatrix}. \tag{51}$$

It is straightforward to show that the *composition* of symplectic transformations is symplectic. To see that our methods are symplectic, we break the propagation scheme into four stages as given at the beginning of section 4 and show that each stage is symplectic. For a stage that advances velocity it must be shown that the Jacobian matrix of F^n with respect to X^n is symmetric.

The $\overline{\mathrm{E}}$ form of our method can be made symplectic by defining a velocity or, equivalently, a momentum $\bar{P}$, appropriately. We set up a symplectic transformation from (X, P) to $(\bar{X}, \bar{P})$ and then obtain automatically symplecticness for the transformation from $(\bar{X}^n, \bar{P}^n)$ to $(\bar{X}^{n+1}, \bar{P}^{n+1})$. Half the transformation is, by definition,

$$X = \bar{X} + \alpha \Delta t^2 E_x(\bar{X}); \tag{52}$$

the other half is obtained by using the generalized momenta [31, p. 60] as a conjugate to the changed position coordinates, where

$$\bar{P} = P + \alpha \Delta t^2 E_{xx}(\bar{X}) M^{-1} P. \tag{53}$$

As noted, there appears to be a widespread preference for the $2\overline{\mathrm{E}}$ form. One reason, given by [14], is the feeling that "The discrete propagator in the **q**-space has no prescription for the velocity." (Here **q** is the same as our x.) However, we can insist that for arbitrary Hamiltonian systems the following conditions hold:

1. the method is symplectic when rewritten in terms of position and velocity (with momentum defined as mass times velocity), and
2. the prescription is second-order accurate.

Then there seems to be a unique formula for the velocity. We omit the argument here except to note that it is sufficient to restrict the prescription for velocity to be in terms of X^{n-1} and X^n, since this suffices for generating all other trajectory values.

6. Pre- and postprocessing. Recall that the $\alpha = \frac{1}{12}$ method (Cowell's) is not technically fourth-order accurate unless it is expressed in form $2\overline{\mathrm{E}}$; even then, the fourth-order accuracy applies only to the position values, not the velocity values. This sensitivity to form suggests that the other forms of the numerical scheme actually use values obtained by some transformation of a more accurate solution. Further, it suggests that the position and velocity values used by the scheme can be reinterpreted. Hence, if we suitably "encode" the initial values and reverse this process for the actual computed values, we might get a more accurate solution. This is, in fact, true not only for the choice $\alpha = \frac{1}{12}$ but also for other values of α, though less dramatically.

A reinterpretation of the numerical solution is also suggested by the fact that the M and E forms of a method are intrinsically equally good for long-time solution propagators. Note that this reinterpretation of the numerical values is a theoretical tool for the purposes of comparing methods; it is not necessarily suggested for an actual long-time MD simulation. The minor local improvements in accuracy are of little consequence for long-time integrations. However, they are useful for monitoring energy conservation and *might* be useful for some other computations.

Below we formulate a transformation for pre- and postprocessing the trajectories that will result in a more accurate solution. The transformation is symplectic, guaranteeing that the transformed system of differential equations is also Hamiltonian. Let (X, P) denote the values used by the numerical method and let (x, p) denote transformed values that represent better approximations to the true values. The easiest way to ensure that a transformation is symplectic is to obtain it from a *generating function*. Here we use a generating function of the second kind [31, p. 266]

$$S(X,p) = p^{\mathrm{T}}X + \beta\Delta t^2 p^{\mathrm{T}}M^{-1}E_x(X), \tag{54}$$

where β is a parameter. (This particular transformation was obtained on the basis of experience and trial and error.) The transformation becomes by definition

$$x = S_p(X,p), \quad P = S_x(X,p),$$

or

$$x = X + \beta\Delta t^2 M^{-1}E_x(X), \quad P = p + \beta\Delta t^2 E_{xx}(X)M^{-1}p. \tag{55}$$

The preprocessing, which involves transforming given initial (x, p) values into (X, P) values for the numerical method, requires the solution of a nonlinear system of equations for X. The postprocessing (to get output values (x, p)) requires only that a linear system be solved for p. If we make this change of variables in the Hamiltonians (33) and (34), we get for the E form

$$\begin{aligned}\tilde{H} = {} & \frac{1}{2}p^{\mathrm{T}}M^{-1}p + E(x) \\ & + \Delta t^2\left(\left(\frac{1}{12}+\beta\right)p^{\mathrm{T}}M^{-1}E_{xx}M^{-1}p - \left(\frac{1}{24}+\frac{1}{2}\alpha+\beta\right)(E_x)^{\mathrm{T}}M^{-1}E_x\right) + O(\Delta t^4)\end{aligned}$$

and for the M form

$$\begin{aligned}\tilde{H} = {} & \frac{1}{2}p^{\mathrm{T}}M^{-1}p + E(x) \\ & + \Delta t^2\left(\left(-\frac{1}{24}+\beta\right)p^{\mathrm{T}}M^{-1}E_{xx}M^{-1}p - \left(-\frac{1}{12}+\frac{1}{2}\alpha+\beta\right)(E_x)^{\mathrm{T}}M^{-1}E_x\right) + O(\Delta t^4).\end{aligned}$$

Note that in both cases the effect of nonzero β is to transfer weight from one error term to the other. Thus, we can choose to eliminate the first or second error term [32] or to make their coefficients equal. Making the coefficients equal implies

$$\beta = -\frac{1}{4}\left(\alpha + \frac{1}{4}\right) \qquad \text{(E form)}, \tag{56}$$

$$\beta = -\frac{1}{4}\left(\alpha - \frac{1}{4}\right) \qquad \text{(M form)}. \tag{57}$$

In either case, we then have

$$\begin{aligned}\tilde{H} = {} & \frac{1}{2}p^{\mathrm{T}}M^{-1}p + E(x) \\ & + \frac{1}{4}\left(\frac{1}{12}-\alpha\right)\Delta t^2\left((M^{-1}p)^{\mathrm{T}}E_{xx}M^{-1}p + (E_x)^{\mathrm{T}}M^{-1}E_x\right) + O(\Delta t^4)\end{aligned} \tag{58}$$

and

$$\frac{d}{dt}H = -\frac{1}{4}\left(\frac{1}{12} - \alpha\right)\Delta t^2\left((M^{-1}p)^{\mathrm{T}}E_{xxx}M^{-1}pM^{-1}p\right) + O(\Delta t^4). \tag{59}$$

When the potential is quadratic, the above quantity is $O(\Delta t^4)$. Thus with the appropriate interpretation of the computed values, all methods very nearly conserve energy in the harmonic case. By comparison, without the processing we have for the M form

$$\frac{d}{dt}H = -\frac{1}{24}\Delta t^2\left((M^{-1}p)^{\mathrm{T}}E_{xxx}(M^{-1}p, M^{-1}p)\right) + \left(\frac{1}{4} - \alpha\right)\Delta t^2\left((M^{-1}p)^{\mathrm{T}}E_{xx}M^{-1}E_x\right) + O(\Delta t^4).$$

If we want to apply this transformation in practice, the preprocessing can be approximated by

$$X \approx x - \beta\Delta t^2 M^{-1}E_x(x), \quad P = p + \beta\Delta t^2 E_{xx}(X)M^{-1}p, \tag{60}$$

and the postprocessing by

$$x = X + \beta\Delta t^2 M^{-1}E_x(X), \quad p \approx P - \beta\Delta t^2 E_{xx}(X)M^{-1}P. \tag{61}$$

This transformation can also be approximated by formulas based on the following equations, whose detailed derivation is given in [33]:

$$\begin{aligned} X^n &= x^n + \beta\Delta t^2(x^{n+1} - 2x^n + x^{n-1}) + O(\Delta t^4), \\ P^n &= p^n - \beta\Delta t^2(p^{n+1} - 2p^n + p^{n-1}) + O(\Delta t^4), \end{aligned} \tag{62}$$

with associated postprocessing formulas

$$\begin{aligned} x^n &= X^n - \beta\Delta t^2(X^{n+1} - 2X^n + X^{n-1}) + O(\Delta t^4), \\ p^n &= P^n + \beta\Delta t^2(P^{n+1} - 2P^n + P^{n-1}) + O(\Delta t^4). \end{aligned} \tag{63}$$

These approximations are not symplectic, but that is not necessary for our purpose. Symplecticness helps only if we iterate a map many times, such as we do when we propagate the (encoded) numerical solution.

7. Numerical experiments. The orders of accuracy claimed in this paper have been confirmed for all schemes by numerical experiments (data not shown). To test these ideas of pre- and postprocessing, energetic fluctuations, stability, and accuracy, we performed numerical experiments on a butane molecule with the united-atom representation.[3] The potential energy is composed of bond-length stretching, bond-angle bending, and dihedral angle rotation terms. Model and potential details are given in [6].

In the united-atom representation, the fastest period of the motion is much longer than that of the atomic-level model because hydrogen atoms are not explicitly modeled (instead, groups of CH_2 and CH_3 are considered). An estimate for the highest-frequency timescale for each model can be obtained by the square root of the ratio of characteristic units for mass (m) and the force constant (K) for bond stretching,

[3]Butane has the chemical formula C_4H_{10}, and is described by the linkage $CH_3 - CH_2 - CH_2 - CH_3$.

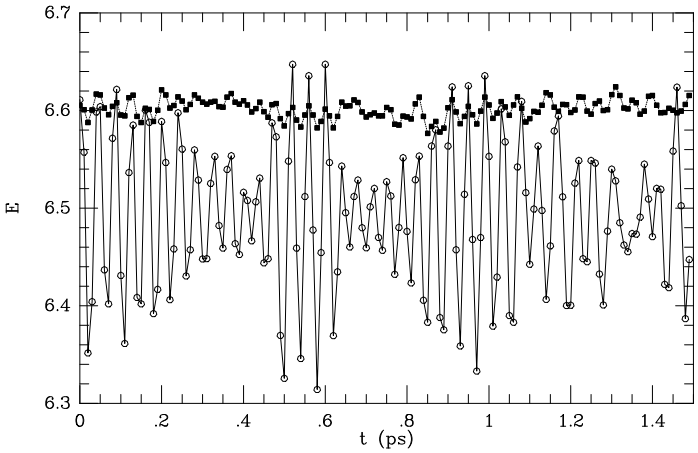

FIG. 2. *Total energy of a butane molecule from velocity Verlet ($\alpha = 0$) dynamics, as obtained by both unprocessed and processed 1E form. Open circles represent the energy evolution from 1E-form dynamics, and filled squares represent the processed 1E-form values with $\beta = -\frac{1}{16}$. The timestep used is 10 fs. The exact value of the energy is its initial value, approximately 6.61.*

i.e., $\tau \approx 2\pi\sqrt{m/K}$. For an all-atom model, $M = 1$ amu (for hydrogen) and $K \approx 400$ kcal/mol/Å^2 and thus $\tau \approx 15$ fs. For a united-atom model, $M = 12$ amu (for CH_2) and $K \approx 80$ kcal/mol/Å^2, so the period τ is about 120 fs. Thus in the latter model, τ is about eight times greater.

Below we use $\Delta t = 10$ fs unless stated otherwise (in all-atom models, typically $\Delta t = 1$ fs is used). All reported results are obtained from simulations of a single molecule started from a local minimum and zero initial velocity. To heat the system to room temperature (300 K), a 20-ps Langevin dynamics simulation is performed [6]. At this point, we switch to Newtonian dynamics.

For $\alpha = 0$ (Verlet method), we plot in Figure 2 the total energy of the butane molecule during the dynamics. The curve with filled squares corresponds to the processed 1E form and that of open circles to the unprocessed 1E form (the velocity Verlet). As predicted, the energy fluctuation in the processed trajectory is much smaller than that of the unprocessed one. Specifically, the rms (root-mean-square) deviation from the mean energy of the processed is about $\frac{1}{10}$ of that of the unprocessed method.

Next, we compare in Figure 3 the evolution of the dihedral angle of butane[4] as a function of time for both the processed and unprocessed versions of the E and M methods for $\alpha = 0$ (Verlet), and $\alpha = \frac{1}{2}$ (LIM2). In each case, forms 1E, 1M, 1E*, and 1M* are given; superscript * denotes processed. It is evident that the processed trajectories are closer to one another for a specific α. This is expected because the processing can make the effective Hamiltonians of forms 1E and 1M the same (up to fourth order in Δt). It ensures that α can be our sole classification parameter for different methods.

Figure 4 shows dihedral angle trajectories for various processed methods in the E form with $\Delta t = 5$, 10, 20, 30 fs, with several choices of α: 0 (Verlet), $\frac{1}{12}$ (Numerov–Cowell), $\frac{1}{4} - \frac{1}{\pi^2}, \frac{1}{4}$ (midpoint), $\frac{1}{2}$ (LIM2). The value from the trajectory integrated with $\Delta t = 1$ fs is shown as a thick solid line for reference. The methods with α=0

[4] A dihedral angle defines the rotation of two atom groups about the bond connecting them. Thus, for butane, τ defines the rotation about the central C-C bond.

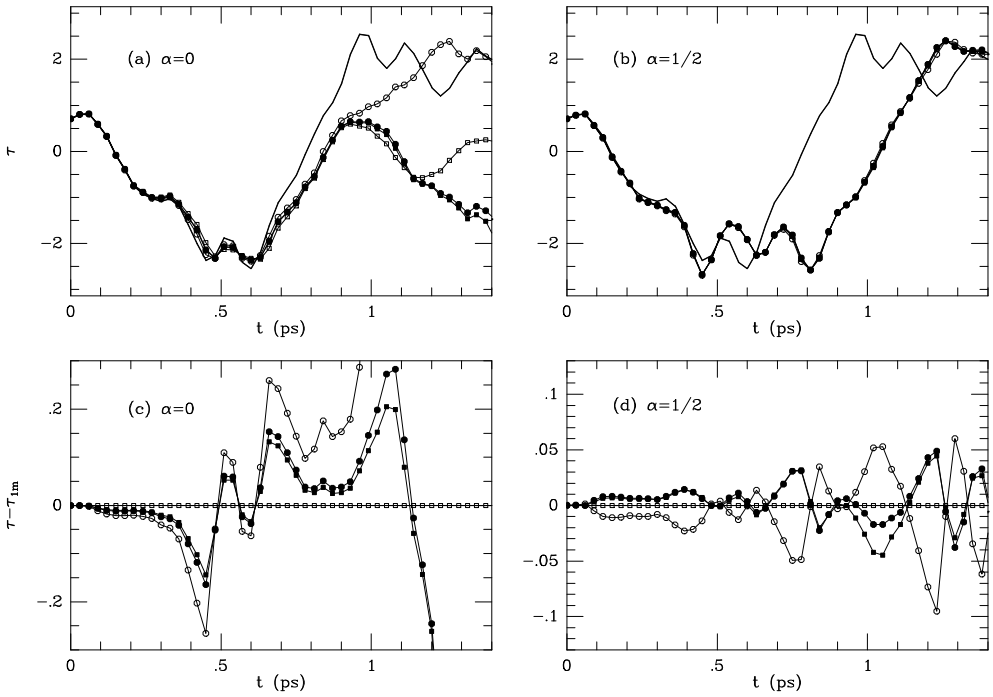

FIG. 3. *The evolution of butane's dihedral angle* τ *for Verlet and LIM*2 *integrators. Parts* (a) *and* (b) *show* τ *trajectories obtained for* $\alpha = 0$ *(Verlet) and* $\alpha = \frac{1}{2}$ *(LIM*2*), respectively, for form* 1*E (open circles), processed* 1*E (filled circles), form* 1*M (open squares), and processed* 1*M (filled square). Parts* (c) *and* (d) *are essentially the same as* (a) *and* (b) *except that the ordinates in* (c) *and* (d) *show the angular difference between the* (a) *or* (b) *values and corresponding* 1*M values. The angular difference are plotted here to make the differences among different forms clear. A timestep of* 10 *fs is used. The solid line in plots* (a) *and* (b) *represents the angle evolution obtained at a timestep of* 1 *fs.*

and $\frac{1}{12}$ are unstable at $\Delta t = 30$ fs, so only curves with $\Delta t = 5$, 10, and 20 fs are shown. Among these methods, Numerov–Cowell has the highest accuracy; in theory, it is fourth-order accurate with the pre- and postprocessing. It is also notable that the trajectories with different timesteps are close to the reference solution within the 1.5 ps simulation length. Other methods produce close trajectories to the solid curve only when $\Delta t \leq 5$ fs, except for the case $\alpha = \frac{1}{4} - \frac{1}{\pi^2}$ which is nearly as accurate for 10 fs also. Beyond 10 fs, it is difficult to pinpoint "better" or "worse" performance.

8. Conclusion. We have unified and defined a group of implicit integrators, differentiated by a single parameter α. One explicit method is also included in the group as a reference and as a special case of the defining parameter ($\alpha = 0$). The basic framework of our integrators is given by the force expression in (10). We showed that $\alpha = 0$ corresponds to the Störmer–Verlet method, $\alpha = \frac{1}{12}$ to Numerov–Cowell, $\alpha = \frac{1}{4}$ to implicit-midpoint (and trapezoid rule), and $\alpha = \frac{1}{2}$ to LIM2 of Zhang and Schlick. It was also shown that these methods are symplectic. Some of the methods have more than one common form, and six forms are presented in section 2.

From analysis of the harmonic oscillator case (linear forces), we showed that schemes with $\alpha < \frac{1}{4}$ impose a condition on the timestep for stability. By deriving explicit propagation formulas for positions and velocities, we showed that the frequency

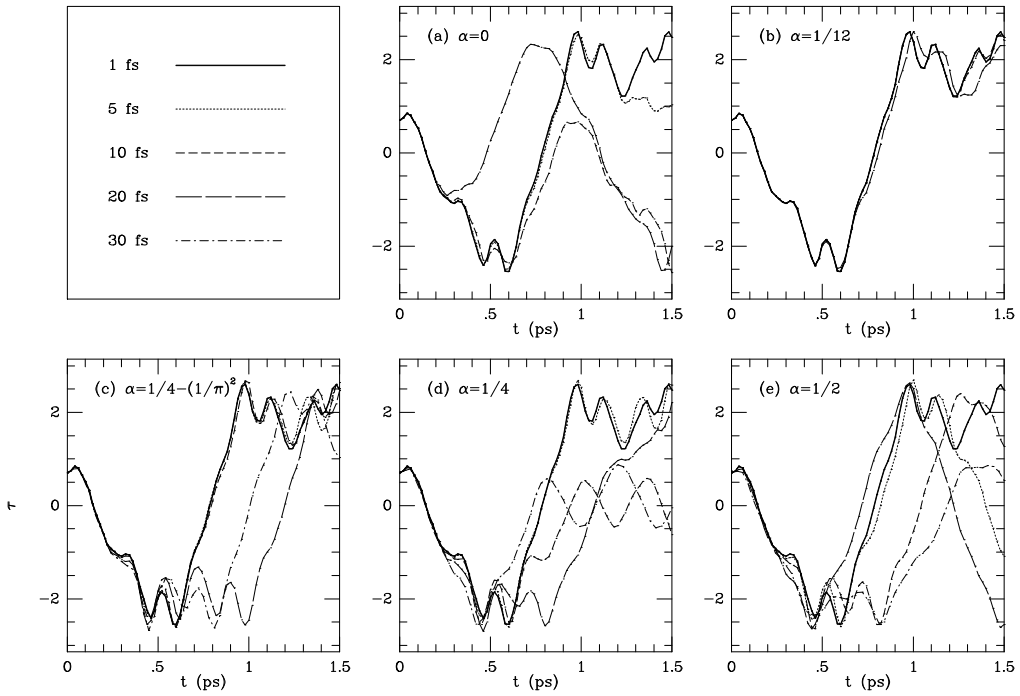

FIG. 4. *Time evolution of the dihedral angle of butane molecule from processed* 1*E-form dynamics. For each method (or* α *value), trajectories are shown for timesteps in the* 1 *fs (solid line) to* 30 *fs range. For* $\alpha = 0$ *(Verlet) and* $\alpha = \frac{1}{12}$ *(Cowell–Numerov), trajectories at* 30 *fs timesteps are unstable and not shown.*

of the oscillator is distorted due to the discretization and that the effective frequency $(\frac{\theta}{\Delta t})$ is timestep, frequency, and method dependent. We illustrated this by showing the dependence of the rotation (θ) on the timestep, frequency, and method. A special value of $\alpha = \frac{1}{4} - \frac{1}{\pi^2}$ was suggested to make this rotation as close as possible to the target value (see Figure 1).

Also, the E and M forms are essentially equivalent in the sense that there exists a canonical transformation that transfers the effective Hamiltonian of either form to a common form (accurate up to fourth order in timestep). This property of different forms allows us to apply special pre- and postprocesses to make the processed E and M forms have close trajectories (see Figure 3).

In our analysis, an α-dependent expression for β is used (see (56), (57)). This choice yields a fourth-order accurate (in Δt) scheme for $\alpha = \frac{1}{12}$ where the second-order term in (58) vanishes and reveals the intrinsic fourth-order accuracy of the Numerov–Cowell method. Furthermore, from (59), better energy conservation can be obtained for the harmonic case. This improves energy conservation even for nonlinear systems since the error from the harmonic part can be reduced significantly.

What might be the practical implications of this work for biomolecular dynamics? The interpretation of discretization errors as a modification to the Hamiltonian method implies that observed energy fluctuations represent a sampling of the perturbation term of the Hamiltonian. Thus *for symplectic integrators* significance can be attached to the size of the fluctuations. And this remains true if a more favorable and "truer" interpretation of the numerical solution is obtained by means of process-

ing based on a *symplectic transformation*. Our analyses and experiments have not resolved the question of whether it is worthwhile to use *conventional* integration formulas other than leapfrog–Verlet. Further investigation is needed into questions of efficient implementation and resonances before conclusions can be reached.

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