On processed splitting methods and high-order actions in path-integral Monte Carlo simulations

Fernando Casas[a)]

Departament de Matemàtiques and Institut de Matemàtiques i Aplicacions de Castelló (IMAC), Universitat Jaume I, E-12071 Castellón, Spain

Processed splitting methods are particularly well adapted to carry out path-integral Monte Carlo (PIMC) simulations: since one is mainly interested in estimating traces of operators, only the kernel of the method is necessary to approximate the thermal density matrix. Unfortunately, they suffer the same drawback as standard, nonprocessed integrators: kernels of effective order greater than two necessarily involve some negative coefficients. This problem can be circumvented, however, by incorporating modified potentials into the composition, thus rendering schemes of higher effective order. In this work we analyze a family of fourth-order schemes recently proposed in the PIMC setting, paying special attention to their linear stability properties, and justify their observed behavior in practice. We also propose a new fourth-order scheme requiring the same computational cost but with an enlarged stability interval. © *2010 American Institute of Physics.*
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I. INTRODUCTION

Splitting methods constitute an important class of numerical integrators for differential equations when they can be separated into two or more parts that are either solvable or simpler to integrate than the original problem. Given the ordinary differential equation

$$\dot{x} = f(x), \quad x_0 = x(t_0) \in \mathbb{R}^D, \tag{1}$$

a one-step numerical *integrator* ψ_h with time step h is said to be of order $\geq r$ if the numerical approximation $x_h \equiv \psi_h(x_0)$ to the exact solution $x(h)$ is such that $x_h = x(h) + \mathcal{O}(h^{r+1})$.

Let us suppose that f can be expressed as $f = f^{[a]} + f^{[b]}$, in such a way that the equations

$$\dot{x} = f^{[a]}(x), \quad \dot{x} = f^{[b]}(x), \quad x_0 = x(t_0) \tag{2}$$

can be exactly integrated, with solutions $\varphi_h^{[a]}(x_0)$ and $\varphi_h^{[b]}(x_0)$ at $t=h$, respectively. Then, a simple calculation shows that

$$\chi_h = \varphi_h^{[b]} \circ \varphi_h^{[a]} \tag{3}$$

provides a first order numerical approximation. This is also true for its adjoint $\chi_h^* = \varphi_h^{[a]} \circ \varphi_h^{[b]}$, whereas the composition

$$\mathcal{S}_h^{[2]} = \varphi_{h/2}^{[a]} \circ \varphi_h^{[b]} \circ \varphi_{h/2}^{[a]} \tag{4}$$

furnishes a second-order numerical scheme, known as leapfrog, Strang or Störmer–Verlet method, depending on the context where it is used. Higher-order approximations can be achieved by composing these flows with appropriately chosen weights a_i, b_i, i.e.,

$$\psi_h = \varphi_{ha_1}^{[a]} \circ \varphi_{hb_1}^{[b]} \circ \varphi_{ha_2}^{[a]} \circ \cdots \circ \varphi_{ha_p}^{[a]} \circ \varphi_{hb_p}^{[b]}. \tag{5}$$

Schemes (5) are called splitting methods. By convention, only the number of evaluations of one of the flows (say, $\varphi_h^{[b]}$) is counted. Thus, the composition (5) is said to be a p-stage method. It is called time-symmetric if in addition $a_i = a_{p+1-i}$, $b_p = 0$, and $b_i = b_{p-i}$.

Splitting methods are frequently used in celestial mechanics, molecular dynamics, quantum and statistical mechanics, and, in general, for solving numerically differential equations in such a way that relevant geometric properties of the vector field f have to be preserved under discretization. It has been in this context and in connection with splitting methods where the processing technique has shown its usefulness.[1,2] The idea of processing, first considered by Butcher for Runge–Kutta methods,[3] can be summarized as follows: one tries to enhance the integrator ψ_h by a suitable parametric map π_h in such a way that the resulting scheme

$$\hat{\psi}_h = \pi_h \circ \psi_h \circ \pi_h^{-1} \tag{6}$$

is of order higher than ψ_h. The method ψ_h is called the kernel and π_h is known as the (post)processor or corrector of the *processed* method $\hat{\psi}_h$. Application of n steps of the integrator $\hat{\psi}_h$ leads to

$$\hat{\psi}_h^n = \pi_h \circ \psi_h^n \circ \pi_h^{-1}.$$

Observe that the *preprocessor* π_h^{-1} is applied only once, so that its computational cost may be ignored, then the kernel ψ_h acts once per step and finally the action of the postprocessor π_h is evaluated only when output is required. This technique is of course advantageous if $\hat{\psi}_h$ is a more accurate method than ψ_h and the cost of π_h is negligible: it provides the accuracy of $\hat{\psi}_h$ at the cost of the less accurate method ψ_h.

One says that the method ψ_h is of *effective order* r if a

a)Electronic mail: fernando.casas@uji.es.

postprocessor π_h exists for which $\hat{\psi}_h$ is of (conventional) order r,[3] that is

$$\pi_h \circ \psi_h \circ \pi_h^{-1}(x_0) = x(h) + \mathcal{O}(h^{r+1}). \qquad (7)$$

A simple example of a processed splitting method is, in fact, the Störmer–Verlet method (4). As a consequence of the group property of the exact flow, we have

$$\begin{aligned}
\mathcal{S}_h^{[2]} &= \varphi_{h/2}^{[a]} \circ \varphi_h^{[b]} \circ \varphi_{h/2}^{[a]} = \varphi_{h/2}^{[a]} \circ \varphi_h^{[b]} \circ \varphi_h^{[a]} \circ \varphi_{-h}^{[a]} \circ \varphi_{h/2}^{[a]} \\
&= \varphi_{h/2}^{[a]} \circ \chi_h \circ \varphi_{-h/2}^{[a]} = \pi_h \circ \chi_h \circ \pi_h^{-1},
\end{aligned} \qquad (8)$$

with $\pi_h = \varphi_{h/2}^{[a]}$. In other words, the basic integrator (3) is of effective order 2.

Processed integrators whose kernel is a splitting method present additional advantages. In general, to achieve order r it is necessary to solve numerically a system of nonlinear polynomial equations in the coefficients (the order conditions), whose number and complexity grow very rapidly with r. Numerically finding every solution and eventually determining the optimal solution turns into a very complicated task for nonprocessed methods, even for relatively small orders. However, when analyzing the order conditions to be verified by $\hat{\psi}_h$, it has been shown that many of them can be satisfied by using π_h,[1,4] so that ψ_h must fulfill a much reduced set of constraints. This allows us to take kernels of effective order r involving far fewer function evaluations than a conventional integrator of order r. Moreover, the map π_h can be approximated in a computationally cheap way by reusing the intermediate stages of the kernel.[4]

As is well known, splitting schemes (5) of order $r \geq 3$ have necessarily some negative coefficients. In other words, the methods always involve stepping backward in time. This constitutes a serious drawback in several applications, for instance, in partial differential equations involving unbounded operators.[5] Also in path-integral Monte Carlo (PIMC) simulations, where splitting methods have been widely used, this property leads indeed to an order barrier, since only positive coefficients must be present in the composition. The typical procedure to circumvent this fundamental difficulty in some particular cases is to introduce modified flows into Eq. (5). In that way, it is possible to construct fourth-order schemes containing only positive coefficients, whereas achieving higher orders requires, in general, the introduction of other more involved flows.

Since in PIMC one is mainly interested in computing traces of quantum operators, it turns out that processed splitting methods are well suited, in particular, the kernel. As a matter of fact, the widely used Takahashi–Imada action[6] is nothing but the kernel of a fourth-order processed method. When higher accuracy is required in the simulations one has to consider higher-order actions. Recently, a two-parameter family of schemes of order 4 containing only positive coefficients first presented in Ref. 7 has been implemented in the path-integral Monte Carlo algorithm and their main properties analyzed.[8] In particular, based on empirical results, it is claimed that for a certain value of the parameters they provide a sixth-order approximation of the energy.[8]

It is the purpose of this paper to present a theoretical justification of this claim and propose new schemes offering a better accuracy for larger values of the time step. We also analyze in detail the relevant problem of constructing fourth-order splitting methods of effective order 6 with all the coefficients being positive. The paper is organized as follows. In Sec. II we review the main results concerning the presence of negative coefficients in splitting methods of order (or effective order) $r \geq 3$ and introduce the so-called modified potentials. In Sec. III we introduce the family of methods analyzed in Ref. 8 in the context of path-integral Monte Carlo simulations. In Sec. IV we carry out a theoretical study of different families of fourth-order schemes and explain why no methods of effective order 6 involving modified potentials with positive coefficients have been constructed so far. Finally, Sec. V contains some concluding remarks.

II. NEGATIVE COEFFICIENTS IN PROCESSED METHODS

The existence of negative coefficients (or backward fractional time steps) in splitting methods of order greater than two is indeed unavoidable, as shown in Refs. 9–11. It can be established as a general theorem:

Theorem 1: *If r is a positive integer such that $r \geq 3$, then for every rth -order method (5) with p any finite positive integer, one has*

$$\min_{1 \leq i \leq p} a_i < 0 \quad \text{and} \quad \min_{1 \leq j \leq p} b_j < 0.$$

The natural question is whether this result also holds for a composition ψ_h of effective order $r \geq 3$. Observe that, in principle, Theorem 1 applies to the whole composition $\hat{\psi}_h = \pi_h \circ \psi_h \circ \pi_h^{-1}$, but it would nonetheless be advantageous to have the negative coefficients restricted only to the composition π_h. For in that case the integration starts by computing π_h^{-1} (which only involves positive coefficients), and then proceeds by evaluating ψ_h (also involving only positive coefficients), whereas π_h introduces only a local error which does not propagate. The answer is provided by the following general result:[12,13]

Theorem 2: *At least one of the a_i as well as one of the b_i coefficients has to be negative in the composition*

$$\psi_h = \varphi_{ha_1}^{[a]} \circ \varphi_{hb_1}^{[b]} \circ \varphi_{ha_2}^{[a]} \circ \cdots \circ \varphi_{ha_p}^{[a]} \varphi_{hb_p}^{[b]}$$

if ψ_h is the kernel of a processed method of order (or equivalently if ψ_h is of effective order) $r \geq 3$.

In certain cases, however, it is possible to circumvent this difficulty and construct schemes of higher order involving only positive coefficients. Let us consider, in particular, the important case of a classical Hamiltonian system of the form $H(q,p) = T(p) + V(q)$, where the kinetic energy $T(p) = \frac{1}{2} p^T M^{-1} p$ for a symmetric square constant matrix M, and the potential $V(q)$ depends only on coordinates. Then $f^{[a]} = \nabla T(p)$ and $f^{[b]} = \nabla V(q)$ in Eq. (1) and denoting by $x = (q,p)^T$, one has

$$\varphi_{ha}^{[a]}(x_0) = (q_0 + ha M^{-1} p_0, p_0),$$

$$\varphi_{hb}^{[b]}(x_0) = (q_0, p_0 - hb\, \nabla V(q_0)). \tag{9}$$

If $\{f^{[a]}, f^{[b]}\}$ denotes the Poisson bracket of the functions $f^{[a]}$ and $f^{[b]}$, then

$$\{f^{[b]}, \{f^{[a]}, f^{[b]}\}\} = -(\nabla V)^T M^{-1}\, \nabla V$$

depends only on q, so that $\{f^{[b]}, \{f^{[b]}, \{f^{[a]}, f^{[b]}\}\}\} = 0$ identically. This introduces additional simplifications in the order conditions and allows one to construct integrators (usually known as Runge–Kutta–Nyström methods) with smaller errors and fewer evaluations.[14] Moreover, the flow corresponding to the "potential" $\{f^{[b]}, \{f^{[a]}, f^{[b]}\}\}$ is explicitly computable and can be included in the integrator. Alternatively, we can replace $\varphi_{hb_i}^{[b]}$ in Eq. (5) when necessary by $\varphi_{h;b_j,c_j}^{[b,c]}$, the flow corresponding to the "modified potential"

$$W_{b_j,c_j} = b_j V(q) - c_j h^2 (\nabla V(q))^T M^{-1}\, \nabla V(q). \tag{10}$$

It acts as

$$\varphi_{h;b_j,c_j}^{[b,c]}(x_0) = (q_0, p_0 - hb_j\, \nabla V(q_0))^T$$
$$+ c_j h^3 (\nabla V(q_0))^T M^{-1}\, \nabla V (q_0)).$$

Methods of this class have been considered in the recent literature.[15–17] Simple examples include the fourth-order scheme[18,19]

$$\psi_h = \varphi_{h/6}^{[b]} \circ \varphi_{h/2}^{[a]} \circ \varphi_{h;2/3,1/72}^{[b,c]} \circ \varphi_{h/2}^{[a]} \circ \varphi_{h/6}^{[b]} \tag{11}$$

and the composition

$$\psi_h = \varphi_{h/2}^{[a]} \circ \varphi_{h;1,1/24}^{[b,c]} \circ \varphi_{h/2}^{[a]}, \tag{12}$$

which is of effective order 4.[6,16] Observe that the inclusion of the new flow allows one to achieve a scheme of order (or effective order) 4 with all the a_i and b_i coefficients being positive. This happens because the coefficients a_i, b_i do not have to satisfy all the order conditions at order $r \geq 3$, and therefore the general Theorems 1 and 2 do not apply here.

Higher-order methods can be constructed along these lines, but they require including other modified potentials of higher degree in h,[13,20] whose evaluation is computationally more costly for a number of problems. In particular, the resulting schemes are not feasible for Monte Carlo simulations. It remains an open problem, however, to determine whether methods of order 4 and *effective* order 6 exist involving only the modified potential (10) with all the a_i and b_i being positive. We will return to this problem in Sec. IV C.

III. PROCESSED METHODS IN PATH-INTEGRAL MONTE CARLO

A. Path-integral Monte Carlo method

As stated in Sec. I, splitting methods involving only positive coefficients are particularly appropriate for PIMC simulations. The PIMC method allows for the calculation of the quantum-statistical partition function, and from it, to estimate other relevant quantities such as the internal energy or the specific heat.[21]

All static and dynamical properties of a quantum system described by a Hamiltonian $\mathcal{H}$ in thermal equilibrium at temperature T can be obtained in principle from the thermal density matrix

$$\rho = e^{-\beta \mathcal{H}},$$

where $\beta = 1/(k_B T)$ and k_B is the Boltzmann constant. Thus, the expectation value for some operator $\hat{O}$ corresponding to a physical observable O, for a system of N quantum particles in a volume V, is given by

$$\langle \hat{O} \rangle = Z^{-1}\, \mathrm{Tr}(\exp(-\beta\mathcal{H})\hat{O}) = Z^{-1} \sum_n \langle n|\exp(-\beta\mathcal{H})\hat{O}|n\rangle, \tag{13}$$

where Z is the partition function

$$Z = \mathrm{Tr}(e^{-\beta\mathcal{H}}) = \sum_n \langle n|e^{-\beta\mathcal{H}}|n\rangle, \tag{14}$$

and the states $|n\rangle$ form a complete, orthonormal basis set.[21,22] Since the eigenvalues of the Hamiltonian $\mathcal{H}$ are not generally known, one tries to evaluate the traces in Eqs. (13) and (14) without diagonalizing the Hamiltonian. This can be done with the Feynman path-integral approach. To proceed, one considers the position representation where the particles are labeled. Then the density matrix is given by

$$\rho(\mathbf{R}, \mathbf{R}'; \beta) \equiv \langle \mathbf{R}|e^{-\beta\mathcal{H}}|\mathbf{R}'\rangle,$$

where $\mathbf{R} \equiv \{\mathbf{r}_1, \ldots, \mathbf{r}_N\}$ and $\mathbf{r}_i$ is the position of the ith particle and the elements of $\rho(\mathbf{R}, \mathbf{R}'; \beta)$ are positive and can be interpreted as probabilities. The partition function then reads

$$Z = \int d\mathbf{R} \langle \mathbf{R}|e^{-\beta\mathcal{H}}|\mathbf{R}\rangle \equiv \int d\mathbf{R}\, \rho(\mathbf{R}, \mathbf{R}; \beta). \tag{15}$$

The following trivial property of the density matrix is the basis of the path-integral method:

$$\exp(-\beta\mathcal{H}) = (\exp(-\varepsilon\mathcal{H}))^M, \tag{16}$$

with $\varepsilon = \beta/M$ for any positive integer M. In consequence, the density matrix can be expressed as

$$\rho(\mathbf{R}_0, \mathbf{R}_M; \beta) = \int \cdots \int d\mathbf{R}_1 d\mathbf{R}_2 \cdots d\mathbf{R}_{M-1} \rho(\mathbf{R}_0, \mathbf{R}_1; \varepsilon)$$
$$\times \rho(\mathbf{R}_1, \mathbf{R}_2; \varepsilon) \cdots \rho(\mathbf{R}_{M-1}, \mathbf{R}_M; \varepsilon). \tag{17}$$

Equivalently, the density matrix at a temperature T is expressed in terms of density matrices at a higher temperature MT. The goal is then to construct a sufficiently accurate approximation to the density matrix while minimizing the number of integrals involved in Eq. (17), i.e., the number of *beads M*.

Finally, the partition function (15) can be written as

$$Z = \int \cdots \int d\mathbf{R}_0 d\mathbf{R}_1 d\mathbf{R}_2 \cdots d\mathbf{R}_{M-1} \rho(\mathbf{R}_0, \mathbf{R}_1; \varepsilon)$$
$$\times \rho(\mathbf{R}_1, \mathbf{R}_2; \varepsilon) \cdots \rho(\mathbf{R}_{M-1}, \mathbf{R}_0; \varepsilon), \tag{18}$$

where the first $|\mathbf{R}_0\rangle$ and the last $|\mathbf{R}_M\rangle$ elements are identified as required by the trace operations.

In practical applications, one must generally use approximations to ρ. Since $\mathcal{H}$ is a Hermitian operator, it follows that $e^{-\varepsilon\mathcal{H}}$ belongs to the symmetric space of positive definite Hermitian operators,[5] so that suitable approximations to ρ are obtained by using symmetric compositions.

Typically, the Hamiltonian is split into two pieces,

$$\mathcal{H} = \hat{K} + \hat{V} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 + \hat{V}, \qquad (19)$$

$\hat{V}$ being the potential. Since the density matrices corresponding to $\hat{K}$ and $\hat{V}$ can be computed explicitly in position space, it makes sense to approximate $e^{-\varepsilon\mathcal{H}}$ by symmetric products of $e^{-\varepsilon\hat{K}}$ and $e^{-\varepsilon\hat{V}}$. The simplest approximation is given, of course, by

$$e^{-\varepsilon(\hat{K}+\hat{V})} \simeq e^{-\varepsilon\hat{K}}e^{-\varepsilon\hat{V}}, \qquad (20)$$

known in this setting as the *primitive action* (PA), in which case

$$\rho(\mathbf{R}_0,\mathbf{R}_2;\varepsilon) \approx \int d\mathbf{R}_1\langle\mathbf{R}_0|e^{-\varepsilon\hat{K}}|\mathbf{R}_1\rangle\langle\mathbf{R}_1|e^{-\varepsilon\hat{V}}|\mathbf{R}_2\rangle.$$

The operator $\hat{V}$ is diagonal in the position representation, whereas the kinetic matrix can be evaluated by using the eigenfunction expansion of $\hat{K}$.[22] It is then possible to arrive at the discrete path-integral expression for the density matrix in the primitive approximation,

$$\rho(\mathbf{R}_0,\mathbf{R}_M;\beta)$$
$$= \int\cdots\int d\mathbf{R}_1 d\mathbf{R}_2\cdots d\mathbf{R}_{M-1}\left(\frac{m}{2\pi\varepsilon\hbar^2}\right)^{3NM/2}$$
$$\times\exp\left(-\sum_{j=1}^{M}\left(\frac{m}{2\varepsilon\hbar^2}\|\mathbf{R}_{j-1}-\mathbf{R}_j\|^2 + \varepsilon\hat{V}(\mathbf{R}_j)\right)\right). \qquad (21)$$

Thus, the density matrix can be calculated at any temperature from an integral over the path $(\mathbf{R}_0,\mathbf{R}_1,\ldots,\mathbf{R}_M)$. Notice that although the primitive action does not provide a symmetric approximation, it can be sometimes evaluated analytically. Moreover, as we have already seen, it is of effective order 2 in $\varepsilon = \beta/M$.

B. Higher-order actions

The simple scheme (21) might suffice to study semiclassical systems in which quantum effects are comparatively small. However, if the interest lies in a fully quantum regime at very low temperatures, to get a sufficiently accurate approximation, the number of beads M increases very fast and the efficiency of the simulation suffers accordingly. On the other hand, it is also desirable to have symmetric compositions to get an approximation in the correct symmetric space of positive definite Hermitian operators. Thus, in the study of fully quantum fluids and solids one is led to consider higher-order approximations to the exponential of the Hamiltonian. As we know, this can be achieved with symmetric factorizations of the form

$$e^{h(\hat{K}+\hat{V})} \simeq \prod_{i=1}^{p} e^{a_i h\hat{K}}e^{b_i h\hat{V}}, \qquad (22)$$

where $h \equiv -\varepsilon$ here plays the role of the time step and the parameters $\{a_i,b_i\}$ are determined according to the required order of accuracy of the approximation. In the Monte Carlo implementation of Eq. (22), all these parameters must be positive. Only in this way the statistical distribution law in the multidimensional integral defining Z is positive definite and can be normalized as a probability distribution which can be sampled by standard Metropolis Monte Carlo methods.

Observe that the approximation (22) is nothing but a reformulation of scheme (5), where now the flows $\varphi_h^{[a]}$ and $\varphi_h^{[b]}$ correspond to the linear operators $\exp(h\hat{K})$ and $\exp(h\hat{V})$, respectively. As usual, in this setting the Poisson bracket $\{f^{[a]},f^{[b]}\}$ has to be replaced by the commutator $[\hat{K},\hat{V}]$.

Since only positive a_i, b_i are permitted in Eq. (22), to achieve approximations of higher order than two in ε, according to the discussion in Sec. II, it is then necessary to introduce new terms incorporating the double commutator $[\hat{V},[\hat{K},\hat{V}]]$. It is worth noting that this commutator only involves a force square term (equivalently, the square of the gradient of $\hat{V}$) as in the classical case. Thus, in particular, one could use the fourth-order scheme (11) also in this setting. Moreover, since we are mainly interested in computing traces of quantum operators [i.e., the expectation value (13) and the partition function Z] and the trace is invariant under similarity transformations, we may consider only the kernel of a processed scheme to approximate $e^{-\beta\mathcal{H}}$. For instance, if the kernel is taken as the composition (12), then the trace is accurate up to fourth-order. This indeed yields the so-called Takahashi–Imada action (TIA),[6] which significantly improves the accuracy of the PA in path-integral Monte Carlo simulations, but not enough to deal properly with fully quantum fluids.[8] To achieve a better degree of accuracy it is necessary of course to work directly with higher-order actions. In particular, compositions (22) with modified potentials of order 4 and effective order 6 containing only positive $\{a_i,b_i\}$ coefficients would be extremely useful here.

In Ref. 8, the family of fourth-order symmetric kernels

$$\psi_h = e^{ha_1\hat{K}}e^{h\hat{W}_{b_1,c_1}}e^{ha_2\hat{K}}e^{h\hat{W}_{b_2,c_2}}e^{ha_2\hat{K}}e^{h\hat{W}_{b_1,c_1}}e^{ha_1\hat{K}} \qquad (23)$$

with modified potential

$$\hat{W}_{b_i,c_i} = b_i\hat{V} + c_i h^2[\hat{V},[\hat{K},\hat{V}]] \qquad (24)$$

has been implemented in the path-integral Monte Carlo algorithm to simulate three different systems: the one-dimensional harmonic oscillator, a drop of H_2 molecules, and bulk liquid ^{4}He as typical test benches for the method. The evaluation of the density matrix of each step $\rho(\mathbf{R}_j,\mathbf{R}_{j+1};\varepsilon)$ has the same complexity as that corresponding to the TIA approximation, and so the computation of the total and partial energies of the system is similar to the ones derived with the Takahashi–Imada action.[8]

The coefficients of the scheme (23) can be expressed in terms of two parameters α, t_0 as

$$a_1 = t_0, \quad b_1 = \frac{1}{6(1-2t_0)^2}, \quad c_1 = u_0\alpha,$$

$$a_2 = \tfrac{1}{2} - t_0, \quad b_2 = 1 - 2b_1, \quad c_2 = u_0(1-2\alpha),$$

$$u_0 = \frac{1}{12}\left(1 - \frac{1}{1-2t_0} + \frac{1}{6(1-2t_0)^3}\right), \qquad (25)$$

so that all the order conditions up to order 4 are automatically satisfied, whereas the values of α, t_0 are restricted to fulfill the conditions

$$0 \le \alpha \le \frac{1}{2}, \quad 0 \le t_0 \le \frac{3-\sqrt{3}}{6} \qquad (26)$$

to guarantee that all the a_i, b_i are positive. Scheme (23) constitutes a generalization of a fourth-order method previously proposed in Ref. 23, which corresponds to $\alpha=0$ and was first considered in Ref. 7.

The presence of two free parameters makes possible to minimize some of the sixth-order error terms and thus render more efficient schemes. Numerical simulations carried out in Ref. 8 show that the required number M in Eq. (16) to reproduce the exact energy of the system at low temperatures is much smaller with scheme (23) than with the primitive action (20) and the Takahashi–Imada method (12). In addition, an empirical procedure is proposed for adjusting α and t_0 to improve the accuracy in the determination of the energy from fourth-order to sixth order. The corresponding error is minimized by taking $\alpha=0.33$ and $t_0=0.1215$ for the harmonic oscillator, whereas for the more complex systems formed by H_2 drops and liquid ^4He a sixth-order is also noticed for a more restrictive interval of values of ε.

This behavior, then, calls for a detailed general analysis of the family of methods of the form (23) with the aim of (i) providing a sound theoretical explanation of the observed phenomena taking place in the simulations and (ii) constructing new schemes offering a better efficiency on an enlarged range of values of ε.

IV. ANALYSIS OF A FAMILY OF FOURTH-ORDER ACTIONS

A. Order conditions

In the following we try to build splitting methods of the form (5) of order 4 and effective order 6 involving the modified potential (24). To simplify our treatment we consider directly the linear setting and analyze the kernel. To carry out as a general treatment as possible, we consider a processed method whose kernel is given by

$$\psi_h = \prod_{i=1}^{p} \exp(a_i h \hat{K}) \exp(h \hat{W}_{b_i, c_i}). \qquad (27)$$

If the scheme is symmetric, then by using the Baker–Campbell–Hausdorff formula[24] it is possible to write formally ψ_h in Eq. (27) as the exponential of an element in the Lie algebra generated by $\hat{K}$, $\hat{V}$, namely,

$$\psi_h = \exp\left(\varepsilon f_{1,1}\hat{K} + \varepsilon f_{1,2}\hat{V} + \varepsilon^3 \sum_{j=1}^{2} f_{3,j}E_{3,j} + \varepsilon^5 \sum_{j=1}^{4} f_{5,j}E_{5,j} \right.$$
$$\left. + \mathcal{O}(\varepsilon^7)\right),$$

where

$$E_{3,1} = [\hat{K},\hat{K},\hat{V}], \quad E_{3,2} = [\hat{V},\hat{K},\hat{V}],$$

$$E_{5,1} = [\hat{K},\hat{K},E_{3,1}], \quad E_{5,2} = [\hat{V},\hat{K},E_{3,1}],$$

$$E_{5,3} = -[\hat{K},\hat{K},E_{3,2}], \quad E_{5,4} = [\hat{V},\hat{V},E_{3,1}],$$

$[\hat{K},\hat{K},\hat{V}] \equiv [\hat{K},[\hat{K},\hat{V}]]$, etc. Here the $f_{i,j}$ are polynomial functions in the coefficients $\mathbf{a} = (a_1, \ldots, a_p)$, $\mathbf{b} = (b_1, \ldots, b_p)$, and $\mathbf{c} = (c_1, \ldots, c_p)$. The order conditions required by a symmetric scheme (27) to be of order 4 are

Order 1: $\quad f_{1,1}(\mathbf{a}) = \sum_{i=1}^{p} a_i = 1, \quad f_{1,2}(\mathbf{b}) = \sum_{i=1}^{p} b_i = 1,$

Order 3: $\quad f_{3,1}(\mathbf{a},\mathbf{b}) = 0, \quad f_{3,2}(\mathbf{a},\mathbf{b},\mathbf{c}) = 0, \qquad (28)$

since order conditions at even order are automatically satisfied. The scheme is of effective order 6 if, in addition,

(I) $\quad f_{5,1}(\mathbf{a},\mathbf{b}) - f_{5,2}(\mathbf{a},\mathbf{b}) = 0,$

(II) $\quad f_{5,3}(\mathbf{a},\mathbf{b},\mathbf{c}) + f_{5,4}(\mathbf{a},\mathbf{b},\mathbf{c}) = 0. \qquad (29)$

In Eqs. (28) and (29) the dependence on the c_i coefficients is always linear, so that the corresponding equations can be satisfied by solving a linear system in $\mathbf{c}$ and only the remaining order conditions involving $\mathbf{a}$ and $\mathbf{b}$ have to be analyzed. This procedure can, of course, be carried out if one has the sufficient number of stages p in the method, and is simplified by introducing the auxiliary quantities

$$s_i \equiv \sum_{j=1}^{i} a_j, \quad s_0 \equiv 0, \quad s_p = 1, \qquad (30)$$

so that

$$\sum_{k=i+1}^{j} a_k = s_j - s_i, \quad i = 1, \ldots, p-1; \quad j = 2, \ldots, p.$$

In this way, the previous order conditions (28) and (29) involving only a_i and b_i coefficients read explicitly

$$f_{12} = 1 \Rightarrow \sum_{i=1}^{p} b_i = 1, \qquad (31)$$

$$f_{31} = 0 \Rightarrow \sum_{i=1}^{p} s_i^2 b_i = \frac{1}{3}, \qquad (32)$$

$$f_{51} - f_{52} = 0 \Rightarrow G_1 \equiv \sum_{i=1}^{p} s_i^4 b_i - \frac{1}{3} \sum_{i=1}^{p-1} \sum_{j=i+1}^{p} (s_j - s_i)^3 b_i b_j$$

$$- \frac{1}{60} = 0, \tag{33}$$

with the additional condition $s_p = 1$. Observe that all the a_i coefficients are non-negative as long as $s_0 = 0 \leq s_1 \leq s_2 \leq \cdots \leq s_p = 1$.

Two types of symmetric compositions may be considered:

(i) ABA-compositions, in which the coefficients are arranged as in method (23). In that case, symmetry imposes the following constraints on the variables in Eqs. (31)–(33):

$$b_p = 0, \quad b_{p-i} = b_i, \quad s_{p-i} = 1 - s_i, \quad c_p = 0, \quad c_{p-i} = c_i.$$

(ii) BAB-compositions, when the first and last flows in the scheme are the one associated with the modified potential. The variables in Eqs. (31)–(33) are related as follows:

$$b_{p+1-i} = b_i, \quad s_{p-i} = 1 - s_{i+1}, \quad c_{p+1-i} = c_i.$$

Let us analyze in detail both types of compositions.

1. ABA-methods

The minimum value of p to solve all the necessary order conditions is $p = 4$. This corresponds precisely to the case analyzed in Ref. 8, i.e., to the family of schemes (23). Since $s_2 = 1/2$, $s_3 = 1 - s_1$, and $s_4 = 1$, there are only three variables (b_1, b_2, s_1) to satisfy Eqs. (31)–(33), whereas the remaining conditions ($f_{3,2} = 0$, $f_{5,3} + f_{5,4} = 0$) can be verified with an appropriate choice of c_1 and c_2.

There are three solutions for b_1, b_2, and s_1, but only one is real, corresponding to $s_1 \simeq 0.486\,421\,104\,317\,088\,9 < \frac{1}{2}$. In consequence, $a_1 = s_1 > 0$, $a_2 = \frac{1}{2} - s_1 > 0$. On the other hand, since

$$b_1 = \frac{1}{6(-1 + 2s_1)^2}, \quad b_2 = 1 - 2b_1, \tag{34}$$

when substituting the previous value of s_1 we get $b_1 = 225.974\,718\,668\,186\,936$, $b_2 = -450.949\,437\,336\,373\,872$. In other words, there are methods of effective order 6 with all the coefficients a_i being positive, but at least one b_j is negative.

Suppose we consider, for simplicity, the one-dimensional harmonic oscillator, $\hat{V} = \frac{1}{2}\lambda^2 x^2$. In that case it is quite straightforward to verify that many of the nested commutators involving $\hat{K}$, $\hat{V}$ vanish identically. In particular, $E_{5,1} = E_{5,2} \equiv 0$. In consequence, only equation (II) in Eq. (29) has to be satisfied by a method of order 4 to achieve effective order 6. Equivalently, any ABA-composition with $p = 4$ satisfying Eq. (34) for some $s_1 < 1/2$ leads to a method of effective order 6 as soon as c_1 and c_2 are taken as

$$c_1 = \frac{-1 + 18s_1 - 144s_1^2 + 552s_1^3 - 576s_1^4}{720(-1 + 2s_1)^3(1 - 6s_1 - 12s_1^2 + 24s_1^3)},$$

$$c_2 = \frac{-1 + 18s_1 - 99s_1^2 + 72s_1^3 + 864s_1^4 - 2160s_1^5 + 1440s_1^6}{90(-1 + 2s_1)^3(1 - 6s_1 - 12s_1^2 + 24s_1^3)}. \tag{35}$$

One has then a family of effective order 6 for the harmonic oscillator depending on the parameter s_1, which can be chosen in such a way that all the a_i and b_i parameters are positive. This happens precisely when

$$0 < s_1 < \frac{3 - \sqrt{3}}{6} \simeq 0.211\,324\,8.$$

If, in addition, $s_1 \in (0, 0.132\,024) \cup (0.142\,326, 0.180\,679)$, then c_1 and c_2 are also positive.

This can be rephrased in terms of the parameters (25) as follows. First, notice that $t_0 = s_1$. Then, we have a method of effective order 6 for the harmonic oscillator if, in addition to conditions (25), α and t_0 are related through

$$\alpha = \frac{-1 + 18t_0 - 144t_0^2 + 552t_0^3 - 576t_0^4}{10(-1 + 18t_0 - 108t_0^2 + 168t_0^3 + 576t_0^4 - 1728t_0^5 + 1152t_0^6)}. \tag{36}$$

This equality is obtained by inserting the expression of c_1 given by Eq. (35) into $\alpha = c_1/u_0$.

In summary, the family of schemes considered here corresponds to the composition (23) with parameters verifying Eqs. (25), (35), and (36). If

$$t_0 = s_1 \in (0, 0.132\,024) \cup (0.142\,326, 0.180\,679),$$

then all the coefficients are positive and the schemes are of effective order 6 for the harmonic oscillator.

For the particular value $t_0 = 0.1215$, one gets $\alpha = 0.329\,556$. In consequence, for the parameters taken in Ref. 8 ($t_0 = 0.1215$, $\alpha = 0.33$), scheme (23) almost satisfies the required conditions to be considered a method of effective order 6 for the harmonic oscillator. The remaining parameters read $a_1 = s_1$, $a_2 = 0.3785$, $b_1 \approx 0.290\,842$, $c_1 \approx 0.001\,735\,65$, and $c_2 \approx 0.001\,795\,32$. With this choice, $G_1 \approx 0.166\,142$, so that the composition is no longer of effective order 6 in general. As a matter of fact, for values of s_1 in the interval $0 < s_1 < (3 - \sqrt{3})/6$ the function G_1 decreases from 0.173 148 to 0.161 74. In other words, this method is only of order 4 for general systems and the remaining effective order 6 condition is not verified by approximately the same amount.

If the number of stages p increases to 5, for the general case there is a free parameter, which can be taken as s_2. This parameter can be used for optimizing the scheme, but essentially the same conclusions as before can be drawn: it is possible to get solutions with all the a_i positive, but $b_2 < 0$, and in addition the values of b_1, b_2 are quite large in absolute value.

When $p = 6$ one has two free parameters (e.g., s_1 and s_2) to solve Eqs. (31)–(33), and one additional c_3. These parameters can be chosen to provide positive a_i and smaller values for b_i, but still one of them is necessarily negative.

2. BAB-methods

In this case we also need at least $p=4$ stages to get isolated real solutions, so that the family of schemes in the quantum mechanical setting has the form

$$\psi_h = e^{h\hat{W}_{b_1,c_1}}e^{ha_1\hat{K}}e^{h\hat{W}_{b_2,c_2}}e^{ha_2\hat{K}}e^{h\hat{W}_{b_2,c_2}}e^{ha_1\hat{K}}e^{h\hat{W}_{b_1,c_1}}. \quad (37)$$

Notice that since the last stage at a given step can be concatenated with the first one at the next, the family of schemes (37) requires exactly the same computational effort as Eq. (23) [this is the so-called first-same-as-last (FSAL) property]. One could say, then, that the number of stages in method (37), as well as in Eq. (23), is only three.

Now the variables to analyze are $(b_1, b_2, a_1 = s_2)$ and all the a_i coefficients are positive if $0 < s_2 < 1/2$. It turns out, however, that $s_2 \approx 1.673\,18$ and $s_2 \approx -0.543\,88$ for the two existing real solutions. In addition, $b_2 < 0$ and thus there are no methods of effective order 6 with positive coefficients for a general potential $\hat{V}$. As before, this is no longer true for the harmonic oscillator. A straightforward analysis of Eqs. (31) and (32) shows that it is indeed possible to get a family of effective order 6 schemes in terms of the parameter s_2, with all the a_i and b_i positive, as long as

$$\frac{3-\sqrt{3}}{6} < s_2 < \frac{1}{2}. \quad (38)$$

The parameters of the scheme can be expressed in terms of s_2 as

$$a_1 = s_2, \quad a_2 = 1 - 2s_2,$$

$$b_1 = \frac{1}{2} - b_2, \quad b_2 = \frac{-1}{12(s_2-1)s_2},$$

$$c_1 = (-5 + 78s_2 - 474s_2^2 + 1404s_2^3 - 2088s_2^4 + 1440s_2^5$$
$$- 360s_2^6)/\gamma,$$

$$c_2 = (-5 + 42s_2 - 126s_2^2 + 156s_2^3 - 72s_2^4)/\gamma,$$

$$\gamma = 2880(-1 + s_2)^2 s_2(-1 + 6s_2 - 12s_2^2 + 6s_2^3). \quad (39)$$

The coefficient c_2 is positive in the whole interval (38), whereas $c_1 > 0$ when $s_2 \in (0.211\,325, 0.350\,226) \cup (0.459\,992, 0.5)$.

For a general potential, it turns out that G_1 increases monotonically from 0.161 74 to 0.173 148, and thus one expects the same kind of behavior as with scheme (23).

When $p=5$ there is one free parameter s_2, and one also gets real solutions with all a_i coefficients being positive, but at least one b_j is negative.

B. Linear stability analysis

In addition to the usual order conditions, another feature of a numerical integration method for differential equations is *stability*. Roughly speaking, the numerical solution provided by a stable numerical integrator does not tend to infinity when the exact solution is bounded. Numerical integrators with a large stability interval are particularly suitable to carry out PIMC simulations, since in that context one is

mainly interested in applying methods with as large a step size h as possible to minimize the number of beads M and thus the computational effort required to estimate the multivariate integrals appearing in the scheme. In this respect, notice that solving the order conditions guarantees small errors only in the limit $h \to 0$.

The (linear) stability of the splitting method (5) is typically analyzed by applying the scheme to the classical one-dimensional harmonic oscillator,[25,26]

$$y'' + \lambda^2 y = 0, \quad \lambda > 0, \quad (40)$$

with the standard $(q,p) = (\lambda y, y')$ splitting

$$\begin{pmatrix} q' \\ p' \end{pmatrix} = \left[\underbrace{\begin{pmatrix} 0 & \lambda \\ 0 & 0 \end{pmatrix}}_{A} + \underbrace{\begin{pmatrix} 0 & 0 \\ -\lambda & 0 \end{pmatrix}}_{B} \right] \begin{pmatrix} q \\ p \end{pmatrix}. \quad (41)$$

Since the exact solution is given by the 2×2 matrix,

$$O(x) = \begin{pmatrix} \cos x & \sin x \\ -\sin x & \cos x \end{pmatrix}, \quad x = h\lambda, \quad (42)$$

the idea here is to find the maximal time step (or equivalently the maximal value of x) for which all numerical solutions remain bounded.

When applying the splitting method (27) to Eq. (41), one approximates $O(x)$ in Eq. (42) by

$$K(x) = \begin{pmatrix} 1 & a_1 x \\ 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 \\ -x(b_1 - 2c_1 x^2) & 1 \end{pmatrix} \cdots \begin{pmatrix} 1 & a_p x \\ 0 & 1 \end{pmatrix}$$

$$\times \begin{pmatrix} 1 & 0 \\ -x(b_p - 2c_p x^2) & 1 \end{pmatrix}$$

$$= e^{ha_1\hat{K}}e^{h\hat{W}_{b_1,c_1}} \cdots e^{ha_p\hat{K}}e^{h\hat{W}_{b_p,c_p}}, \quad (43)$$

where now $\hat{K} = A$ and $\hat{W}_{b_i,c_i} = b_i B + c_i h^2 [B,[A,B]]$.

We define the stability threshold x_* as the largest non-negative real number such that $K(x)$ is stable for all $x \in (-x_*, x_*)$. In other words, $[K(x)]^n$ can be bounded independently of $n \geq 1$ for $x \in (-x_*, x_*)$ if all the eigenvalues of K lie on the stability interval $(-x_*, x_*)$. The stability threshold x_* depends on the coefficients $\{a_i, b_i, c_i\}$ of the method (27) and verifies $x_* \leq 2p$, since $2p$ is the maximal value of the stability threshold, which is achieved by the concatenation of p steps of length h/p of the leapfrog scheme.[27]

In terms of the so-called stability polynomial, $p(x) = \frac{1}{2}\text{Tr}\,K(x)$, it is clear that if the method is stable for a given $x \in \mathbb{R}$, then $|p(x)| \leq 1$. In Ref. 28, a practical criterion for estimating x_* has been proposed. Essentially, one has to determine the smallest real positive zero with odd multiplicity of the polynomial $p(x)^2 - 1$.

For processed methods, i.e., schemes of the form (6), it is clear that their linear stability is determined only by the kernel ψ_h, since the eigenvalues are invariant under similarity transformations. In consequence, all the previous considerations are still valid when the kernel of the processed method is the composition (27).

In the sequel we analyze the linear stability of the symmetric kernels (23) and (37). Observe that due to the FSAL property, one may say that the number of stages for both

Method	Parameter	Largest x_*	x_*/p
ABA	$s_1 = 0.1234$	3.0731	1.024 36
BAB	$s_2 = 0.2785$	3.1399	1.046 63

integrators is $p=3$. As we have seen in Sec. IV A, it is possible to design a one-parameter family of schemes with all the coefficients being positive. The idea is now to determine for each family the stability threshold x_* as a function of the free parameter and select the parameter leading to the largest value of x_*. In such a way, we will have a pair of methods of order 4 and effective order 6 for linear systems with maximal stability interval and positive coefficients.

The stability polynomial in both cases has the form

$$p(x) = 1 - \tfrac{1}{2}x^2 + \tfrac{1}{24}x^4 - \tfrac{1}{720}x^6 + \mathcal{O}(x^8),$$

where the dependence on the parameter s_1 [respectively s_2 for method (37)] appears at higher-order terms, beginning in x^8. Notice that $p(x)$ approximates $\cos x$ up to order 6 in accordance with the order of accuracy of the schemes. By analyzing the zeros of the polynomial $p(x)^2 - 1$ as a function of the parameter s_1 (respectively s_2) in the range of values guaranteeing that all the coefficients of the method are positive, one gets the values of x_* collected in Table I.

The values obtained for x_*/p should be compared with 2, which is the maximal stability threshold attained by the leapfrog method (4). Observe that with the BAB composition it is possible to achieve a larger stability interval. In other words, it can be used with a larger step size than the ABA method (23).

The scheme (23) with the maximal stability interval corresponds then to $t_0 = s_1 = 0.1234$, α given by Eq. (36) and the remaining coefficients determined by Eq. (25), whereas the corresponding BAB-method (37) is obtained from Eq. (39) with $s_2 = 0.2785$. For the sake of comparison, it is worth remarking that for the value $t_0 = 0.1215$ considered in Ref. 8, one has $x_*/p = 1.024\ 19$.

C. On methods of effective order 6 with positive coefficients

From our analysis, it is clear that obtaining fourth-order splitting methods of effective order 6 with all the coefficients a_i, b_i being positive constitutes a particularly elusive problem. Thus, there arises a natural question: Is it possible to *prove* that there are no such methods? This is of course equivalent to show that there are no real solutions of the general equations (31)–(33) with $0 \le s_1 \le \cdots \le s_p = 1$ and $b_i > 0$ for all i.

To simplify the treatment we limit ourselves to symmetric ABA-type compositions with p even, but the extension to other cases is quite straightforward. Equations (31) and (32) read

$$2b_1 + 2b_2 + A = 1,$$

$$(s_1^2 + (1 - s_1)^2)b_1 + (s_2^2 + (1 - s_2)^2)b_2 + B = \tfrac{1}{3}, \quad (44)$$

where

$$A = b_{p/2} + 2 \sum_{i=3}^{p/2-1} b_i,$$

$$B = \frac{1}{4}b_{p/2} + \sum_{i=3}^{p/2-1} (s_i^2 + (1 - s_i)^2)b_i.$$

Solving the linear system (44) in b_1, b_2 we get

$$b_1 = \frac{-1 + 3A - 6B - 6(-1 + A)s_2 + 6(-1 + A)s_2^2}{12(s_1 - s_2)(-1 + s_1 + s_2)},$$

$$b_2 = -\frac{-1 + 3A - 6B - 6(-1 + A)s_1 + 6(-1 + A)s_1^2}{12(s_1 - s_2)(-1 + s_1 + s_2)}. \quad (45)$$

On the other hand, the quadratic form in Eq. (33) can be written as

$$S_3 \equiv \sum_{i=1}^{p-1} \sum_{j=i+1}^{p} (s_j - s_i)^3 b_i b_j = X^T N X \quad (46)$$

in terms of $X^T = (b_1 \cdots b_{p/2})$ and the symmetric matrix N with entries

$$n_{ij} = \begin{cases} (1 - 2s_i)^3 & i = j, \ i = 1, \dots, p/2 - 1 \\ (s_j - s_i)^3 + (1 - s_j - s_i)^3 & i \ne j, \ i,j = 1, \dots, p/2 - 1 \\ \left(\frac{1}{2} - s_i\right)^3 & i = 1, \dots, p/2 - 1, \ j = p/2 \\ 0 & i = j = p/2. \end{cases}$$

In other words,

$$S_3 = (1 - 2s_1)^3 b_1^2 + 2((s_2 - s_1)^3 + (1 - s_2 - s_1)^3)b_1 b_2$$

$$+ (1 - 2s_2)^3 b_2^2 + 2b_1 \sum_{j=3}^{p/2-1} ((s_j - s_1)^3 + (1 - s_j - s_1)^3)b_j$$

$$+ 2\left(\frac{1}{2} - s_1\right)^3 b_1 b_{p/2} + 2b_2 \sum_{j=3}^{p/2-1} ((s_j - s_2)^3$$

$$+ (1 - s_j - s_2)^3)b_j + 2\left(\frac{1}{2} - s_2\right)^3 b_2 b_{p/2} + C, \quad (47)$$

where C involves only the remaining variables $b_3, \dots, b_{p/2}$. Now the argument proceeds as follows. When x_1 and x_2 given by Eq. (45) are substituted into Eq. (47), then S_3 can be factorized as

$$S_3 = \frac{f_s}{12(s_1 - s_2)(-1 + s_1 + s_2)},$$

where f_s has three terms depending again on $\beta \equiv ((s_1 - s_2) \times (-1 + s_1 + s_2))^{-1}$ [those coming from b_1^2, $b_1 b_2$, and b_2^2 in Eq. (47)]. The effective order condition (33) can then be rewritten as

$$s_1^4 \alpha_1 + s_2^4 \alpha_2 + 12(s_1 - s_2)(-1 + s_1 + s_2)\sum_{i=3}^{p} s_i^4 b_i - \frac{1}{3} f_s$$

$$= \frac{1}{5}(s_1 - s_2)(-1 + s_1 + s_2), \qquad (48)$$

where, for simplicity, we have introduced $b_i = \alpha_i \beta$. Real solutions of Eq. (48) with $s_i < s_{i+1}$ correspond to values of s_1, s_2 with $s_1 \approx s_2$ and s_1, s_2 in a neighborhood of 1/2, but when $s_1 \approx s_2$, equations (45) clearly show that either b_1 or b_2 are negative. In other words, there are no solutions with all the coefficients $b_i > 0$.

V. CONCLUDING REMARKS

Splitting methods of order $r \geq 3$ have necessarily some negative coefficients. This is also true for compositions of the form (5) of effective order higher than two, i.e., for kernels of processed schemes of order $r \geq 3$. As we have seen, one way to circumvent this order barrier is by incorporating modified potentials into the composition when the algebraic structure of the problem is suitable. One such setting takes place in path-integral Monte Carlo simulations of quantum systems described by a Hamiltonian operator of the form (19). Moreover, since one is mainly interested in estimating traces of quantum operators, processed splitting methods are particularly appropriate: only the kernel is necessary to approximate $\exp(-\beta \mathcal{H})$ for a given Hamiltonian $\mathcal{H}$. Here the use of high-order methods is also advantageous as long as their relative stability intervals are not too small (thus allowing large step sizes or equivalently, a small number of beads), and, of course, the coefficients are positive.

Recently, the fourth-order splitting method (23) belonging to this class has been used for the first time in several path-integral Monte Carlo simulations.[8] By empirically adjusting two free parameters, it was observed that the scheme behaves in practice as a method of effective order 6, even for complex systems such as H_2 drops and liquid ^{4}He.

In this paper we have carried out a theoretical analysis of this family of methods using standard techniques of the numerical analysis of splitting methods for the integration of differential equations. Thus, we have paid special attention to the required order conditions to achieve order 6 and linear stability properties with the goal of (a) providing a sound justification of the observations reported in Ref. 8 and (b) designing, if possible, new methods within this family with better properties. Thus, we have shown that whereas method (23) satisfies all the order conditions to be of effective order 6 for the harmonic oscillator when Eq. (36) is satisfied, this is not the case for more general systems, since a specific order condition at effective order 6 requires the presence of at least one negative coefficient. As a consequence, the fourth-order method reported in Ref. 8 is only of effective order 6 for the harmonic oscillator and not for a more general potential. Nevertheless, for the special values of the parameters considered in Ref. 8, one has a scheme with a near optimal linear stability interval, and this could explain the observed phenomena.

On the other hand, by reverting the sequence of application of the kinetic and potential parts, we have presented another fourth-order method of effective order 6 requiring the same computational effort but possessing a larger stability threshold, so that it can be used with a larger time step.

From our analysis and the behavior observed in practical simulations in Ref. 8, we may conclude that at least in this setting, it is not strictly necessary to satisfy exactly all the effective order conditions at order 6 for a method to behave in practice as an effective order 6 integrator. In fact, it seems more important for a method (i) to involve only positive coefficients, (ii) to have as large as possible a linear stability interval, and (iii) to satisfy all the effective order conditions in the linear case. If these conclusions are valid, one might design new integration methods by introducing more stages than strictly necessary to verify all the order conditions (e.g., $p = 5$ or $p = 6$) and then use the extra parameters thus introduced to fulfill effective order conditions at higher orders for the linear case, whereas keeping all the coefficients positive and ensuring a large stability threshold. The new methods thus constructed could possibly be competitive with other high-order schemes recently considered in the literature[29] for this type of problems.

ACKNOWLEDGMENTS

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