Propagators for Quantum-Classical Models: Commutator-Free Magnus Methods

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ABSTRACT: We consider the numerical propagation of models that combine both quantum and classical degrees of freedom, usually, electrons and nuclei, respectively. We focus, in our computational examples, on the case in which the quantum electrons are modeled with time-dependent density-functional theory, although the methods discussed below can be used with any other level of theory. Often, for these so-called quantum-classical molecular dynamics models, one uses some propagation technique to deal with the quantum part and a different one for the classical equations. While the resulting procedure may, in principle, be consistent, it can however spoil some of the properties of the methods, such as the accuracy order with respect to the time step or the preservation of the geometrical structure of the equations. Few methods have been developed specifically for hybrid quantum-classical models. We propose using the same method for both the quantum and classical particles, in particular, one family of techniques that proves to be very efficient for the propagation of Schrödinger-like equations: the (quasi)-commutator free Magnus expansions. These have been developed, however, for linear systems, yet our problem is nonlinear: formally, the full quantum-classical system can be rewritten as a nonlinear Schrödinger equation, i.e., one in which the Hamiltonian depends on the system itself. The Magnus expansion algorithms for linear systems require the application of the Hamiltonian at intermediate points in a given propagating interval. For nonlinear systems, this poses a problem as this Hamiltonian is unknown due to its dependence on the state. We approximate it by employing a higher order extrapolation using previous steps as input. The resulting technique can then be regarded as a multistep technique or, alternatively, as a predictor corrector formula.

$$\Gamma(H)=\prod_k \exp[-i\Delta t\sum_\mu \gamma_{k\mu}H(\tau_\mu)]$$
$$y(t+\Delta t)=\Gamma(H)y(t)$$
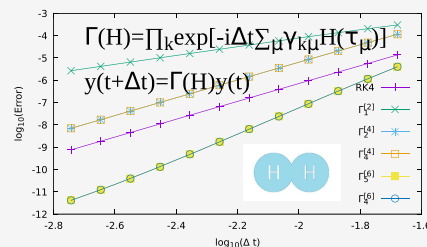
1. INTRODUCTION

Molecular dynamics[1] (MD) has become a well established field since its inception in the 1950s.[2,3] The fundamental assumption of MD, at least in its most conventional definition, is that the atoms are considered to be classical particles, moving in force fields that somehow incorporate the quantum nature of the electrons. Therefore, MD is concerned with the integration of the classical Hamiltonian equations of motion. When the force fields are pre-established, one normally speaks of "classical" MD, whereas if the forces on the nuclei are computed "on the fly" via the first-principles solution of the quantum electronic problem, the term "ab initio", or first principles MD, is used. In both cases, the dynamical problem only concerns the classical nuclei: the electrons merely adapting adiabatically to the ground state corresponding to each instantaneous nuclear configuration. However, if the electronic excited states play a role, one needs a nonadiabatic version of MD and the dynamical problem is then hybrid, mixing both classical and quantum degrees of freedom that evolve simultaneously and are coupled to each other. In this paper, we focus on the propagation of these hybrid quantum-classical systems,[4,5] in particular, for the case in which the electronic problem is approached with time-dependent density-functional theory (TDDFT),[6,7] although the algorithms described below can be used with any other electronic structure technique.

The two different particle types imply the need to propagate two different sets of equations. Usually, the nuclear movement is orders of magnitude slower than the electronic one and therefore not much attention is payed to the nuclear algorithm: a standard robust choice such as the Verlet[8] propagator is considered to be sufficient.

Regarding the quantum part, typically much more costly, many different options have been explored. After discretization of the spatial variables, the resulting equations are systems of ordinary differential equations (ODEs), for which hundreds of techniques exist. We refer the reader to the refs 9−11 for a general introduction and make a quick summary here (some of the following ideas have been tested in combination with TDDFT[12−23]):

- The methods can be divided into single step (that provide a solution at some time t from the solution at a

single previous time $t - \Delta t$) and multistep (that use information from a number of previous time steps). The latter ones have only recently been explored in this context of electronic wave function dynamics.[15,24]

- The Runge−Kutta (RK) family is the most successful family of general purpose single-step integrators.[25] Also, numerous variations exist: partitioned RK, embedded formulas, extrapolation methods (e.g., the Gragg−Bulirsch−Stoer algorithm[26]), composition techniques,[11,27] the linearly implicit Rosenbrock methods,[10] etc.

- One may also make use of the linear structure of the Schrödinger equation: the solution (in the autonomous case) reduces to the action of an exponential, and one may approximate it with a truncated Taylor expansion,[28] with the Chebyshev,[29] and Krylov polynomial expansions,[30,31] with Leja and Padé interpolations,[32] etc. These ideas may be extended to nonautonomous or even nonlinear Hamiltonians.[33]

- Another way to exploit the typical Schrödinger equation structure (in particular, the division of the Hamiltonian into kinetic and potential parts) is making use of splitting techniques (e.g., Lie-Trotter[34] or Strang[35] splittings), such as with the split operator formula[36] or with more sophisticated formulas.[11,27,37−41]

- If the Hamiltonian contains a linear term (e.g., the kinetic operator) and a nonlinear term (e.g., the TDDFT potential), one can use one of the various techniques that combine explicit and implicit schemes for those terms, respectively. Examples are the implicit−explicit "IMEX" formulas[15,42,43] or the exponential integrators[44−47] (exponential Runge−Kutta, integrating factor, exponential time-differencing, etc.).

- Working on an adiabatic or spectral basis, in various similar manners,[14,16,48−51] has been reported to speed up an underlying method.

- Finally, the formal solution to a (linear) time-dependent quantum problem is a time-ordered exponential for the Hamiltonian. Magnus proved in 1954[52] that it could be substituted by the normal exponential of a different operator, which can be given as a series expansion.[53] This idea has led to a family of techniques, the Magnus series expansion-based integrators, which vary in computational cost and accuracy order. In addition to their possible efficiency, they are good at preserving symmetrical or geometrical properties of the exact solution (e.g., unitarity, symplecticity). This is the family of methods that we concentrate on in the current article.

Usually, one propagator for the classical nuclei is simply combined with any of the previously enumerated choices. While the experience proves that the error caused by this combination of two different methods is typically not large, it is desirable to use a single method for the whole system to assure that the properties of the propagator (symplecticity, time reversal symmetry, stability, order of accuracy, etc.) are conserved. However, few authors have considered the design of specifically hybrid propagators.[54−61]

In this contribution, we approach this problem, focusing on the so-called "self-consistent", "Ehrenfest", or simply "quantum-classical" MD model.[4] One also needs to choose an electronic structure level of theory, and in our case, it is time-dependent density functional theory (TDDFT). We then

rewrite Newton's equations of movement for the nuclei in a nonlinear Schrödinger-like form, and together with the Kohn−Sham equations, we use the recently developed commutator-free Magnus (CFM) expansions[62,63] to propagate the whole system. In a previous work,[24] we found that in the context of TDDFT a fourth order implementation of these integrators has an outstanding performance compared with other well-established integrators, such as the exponential midpoint rule (EMR) or the classical fourth order Runge−Kutta (RK4) propagator. This has been the motivation to extend the previous study to (1) higher-order commutator-free Magnus expansions, in particular, sixth order schemes and (2) hybrid quantum-classical models.

It is important to note that both the Kohn−Sham equations for the electrons and the Newton's equations for the nuclei are generally nonlinear, the former through the Hamiltonian dependence on the electronic density. The resulting hybrid model is therefore also nonlinear and can be formulated as a nonlinear Schrödinger equation. The CFM methods were developed, in principle, for linear systems. They require the application of the Hamiltonian at intermediate points of each propagating interval. If we attempt to apply them for a problem with a nonlinear Hamiltonian, we face the difficulty that this Hamiltonian at intermediate steps is not known, since it depends on the state. While generalizations of the Magnus expansion have been proposed for nonlinear problems, in this work, we have employed a simple linearization method: We use extrapolation of the Hamiltonian from previous propagating steps to predict it at the intermediate points. This effectively turns the method into some kind of multistep explicit unitary propagator and implies the need to save a number of previous positions, velocities, and Hamiltonians of the system.

In Section 2, we discuss the theoretical background of the CFM propagators, as well as the Ehrenfest-TDDFT formalism that we use. In Section 3, we show some numerical results. For that purpose, we have implemented these propagation schemes in the octopus[64,65] code, a general purpose pseudopotential, real-space, and real-time density-functional theory code. We finish the paper in Section 4 discussing the advantages and problems of these methods.

2. THEORY

2.1. Ehrenfest Dynamics. We use Ehrenfest dynamics, a nonadiabatic model for the description of classical-quantum systems. The state of the system is determined by a set of classical position and momentum variables $\{q, p\}$ and by the many-electron wave function Ψ. The system is governed by a Hamiltonian $\hat{H}(q, p)$ that is a linear operator in the quantum Hilbert space but also depends on the nuclear coordinates. The equations of motion are

$$\dot{q}_\alpha = \langle \Psi | \frac{\partial \hat{H}}{\partial p_\alpha} | \Psi \rangle \tag{1a}$$

$$\dot{p}_\alpha = -\langle \Psi | \frac{\partial \hat{H}}{\partial q_\alpha} | \Psi \rangle \tag{1b}$$

$$|\dot{\Psi}\rangle = -i\hat{H}(q, p)|\Psi\rangle \tag{1c}$$

These equations are the result of taking the classical limit to the full Schrödinger equation of a set of particles, for a subset of them.[4]

For N-electron problems, however, the size of the wave function grows exponentially with the number of electrons, and the computational cost of managing the full object grows with it. Therefore, one either needs to restrict its size by constraining the many-electron Hilbert space (which leads to the Hartree–Fock, post-Hartree–Fock, configuration-interaction, coupled-cluster, etc. techniques), or alternatively swapping the wave function by the electronic density as the basic variable, i.e., using TDDFT, the choice that we make here. In essence, the idea is to substitute the fully interacting electronic system with a fictitious noninteracting one, which nevertheless has the same density, an object from which in principle (not always in practice) any observable can be extracted. The fictitious noninteracting system can be described with a single Slater determinant formed by N one-electron orbitals $\varphi = \{\varphi_i\}_{i=1}^N$, from which the density can be obtained as

$$n(\vec{r}, t) = \sum_{i=1}^{N} \sum_{\sigma=\uparrow,\downarrow} |\varphi_i(\vec{r}\sigma, t)|^2 \tag{2}$$

where σ runs over the two possible spin indices. The equations of motion for these orbitals are the time-dependent Kohn–Sham equations, a set of one-electron nonlinear Schrödinger-like equations that depend on a density-dependent potential whose precise form has to be approximated. When coupled with the classical nuclei, the resulting Ehrenfest-TDDFT model is

$$i\frac{d}{dt}|\varphi_i\rangle = \hat{H}_{KS}(q, \varphi, t)|\varphi_i\rangle \tag{3a}$$

$$\dot{q}_\alpha = \frac{1}{m_\alpha}p_\alpha \tag{3b}$$

$$\dot{p}_\alpha = F_\alpha[q(t), \varphi(t), t] \tag{3c}$$

The latin index i runs over the N electrons of the system; the greek index α runs over the classical coordinates q_α and p_α; m_α are the nuclear masses, F_α is the force associated to each classical degree of freedom; and $\hat{H}_{KS}(q, \varphi, t)$ is the Kohn–Sham Hamiltonian (that typically depends on the position but not the momenta of the nuclei and on the KS orbitals φ). These last two objects are given by

$$\langle r\sigma|\hat{H}_{KS}(q(t), \varphi(t), t)|\varphi_i(t)\rangle$$
$$= -\frac{1}{2}\nabla^2\varphi_i(r\sigma, t) + v_{ext}(r, q(t), t)\varphi_i(r\sigma, t)$$
$$+ v_{Hxc}[n(t)](r)\varphi_i(r\sigma, t) \tag{4}$$

$$F_\alpha[q(t), \varphi(t), t] = -\sum_i \langle\varphi_i(t)|\frac{\partial\hat{H}_{KS}}{\partial q_\alpha}|\varphi_i(t)\rangle$$
$$- \frac{\partial}{\partial q_\alpha}W(q(t)) + F_\alpha^{ext}(t) \tag{5}$$

In these equations, v_{ext} is the external potential seen by the electrons that includes the interaction with the nuclei (typically, Coulomb terms, although in the calculations shown below, these are modified through the use of pseudopotentials[66]) and perhaps an external electromagnetic field; v_{Hxc} is the Hartree, exchange, and correlation potential that depends on the electronic density; $W(q(t))$ is the

nucleus–nucleus interaction potential, and F_α^{ext} includes any external force on the nuclei.

The KS equations are a set of nonlinear equations because the KS Hamiltonian depends on the electronic density, which, in turn, depends on the KS orbitals. In any case, the resulting model, eq 3a–c, is nonlinear, even in the absence of that TDDFT nonlinearity (i.e., eq 1a–c), due to the classical coupling.

Typically, for this type of hybrid quantum-classical equations, one uses a propagator for the classical variables (e.g., the Verlet integrator) and a different one for the quantum ones. It may work, but this naïve combination is only of the second order of accuracy even if each part is solved to higher accuracy.

There have been various proposals for schemes that truly approach the combined system.[54−61] The first step is to regard the two types of systems as members of the same family such that one may apply the same type of methods for both and for the hybrid. The natural choice, in this case, would be to regard the hybrid model as one symplectic (Hamiltonian) system, as both the quantum and classical equations are symplectic, and therefore the combination is a Hamiltonian system, too.[4,67] It is therefore possible to build a Hamiltonian function (using the classical position and momenta variables, and typically using the real and imaginary parts of the quantum wave function coefficients as "quantum" position and momenta variables), and a hybrid bracket, from which to derive the dynamics. One may then apply a method suited for this type of systems. Unfortunately, to go to higher-order schemes, one needs a series of nested Poisson brackets that imply higher order derivatives and time-consuming computations.

The approach that we have taken, in contrast, is to regard the full system as a nonlinear Schrödinger equation, i.e.

$$\dot{y}(t) = -iH(y(t), t)y(t) \tag{6a}$$

$$y(0) = y_0 \tag{6b}$$

If we now consider the system of equations in the extended variables

$$\dot{u}(t) = -iH(v(t), t)u(t), \quad u(0) = y_0 \tag{7a}$$

$$\dot{v}(t) = -iH(u(t), t)v(t), \quad v(0) = y_0 \tag{7b}$$

it has as unique solution $u(t) = v(t) = y(t)$. We can then consider $v(t)$ as the approximation to $y(t)$ and to take $u(t)$ in the equation of $v(t)$ as a time-dependent function. We need to know approximations to $u(t)$ such that the approximations to $H(u(t),t)$ at the required instants by the method, correspond to Hermitian operators to preserve the qualitative properties. If the method used to compute $v(t)$ is of the order s, we only need to know $u(t)$ at the desired instants to be accurate up to order $s − 1$ since the Hamiltonian will be multiplied by a factor Δt, although, in practice, we will use higher order approximations.

The state vector y must include now both the classical and quantum degrees of freedom, i.e.

$$y = \begin{bmatrix} q \\ v \\ \varphi \end{bmatrix} \tag{8}$$

Here, we are using as a shorthand notation q for all nuclear position coordinates, v for all of their velocities, and φ for all

KS orbital coefficients in some basis or representation. The nonlinear Schrödinger equation may then be written as

$$\begin{pmatrix} \dot{q}(t) \\ \dot{v}(t) \\ \dot{\varphi}(t) \end{pmatrix} = -i \begin{pmatrix} H_C(q(t), \varphi(t), t) & 0 \\ 0 & H_{KS}(q(t), \varphi(t), t) \end{pmatrix} \begin{pmatrix} q(t) \\ v(t) \\ \varphi(t) \end{pmatrix}$$

$$(9)$$

The "classical" Hamiltonian matrix H_C is

$$H_C(q(t), \varphi(t), t) = i \begin{pmatrix} 0 & 1 \\ \dfrac{F(q(t), \varphi(t), t)}{mq(t)} & 0 \end{pmatrix}$$

$$(10)$$

Note that to render the classical equations into a "Schrödinger-like" form, we have used a division and multiplication by $q(t)$. Note also that the matrix is block-diagonal: the classical and quantum particles interact with each other only through the definition of their respective Hamiltonians.

2.2. Commutator-Free Magnus Expansion. Given a nonautonomous linear system

$$\dot{y}(t) = -iH(t)y(t) \tag{11a}$$

$$y(0) = y_0 \tag{11b}$$

the solution can be given, in a neighborhood of t, as

$$y(t + \Delta t) = \exp(\Omega(t + \Delta t, t))y(t) \tag{12a}$$

$$\Omega(t + \Delta t, t) = \sum_{k=1}^{\infty} \Omega_k(t + \Delta t, t) \tag{12b}$$

This is the Magnus expansion.[52] The Ω_k terms are defined in terms of multivariate integrals of nested commutators of increasing order (see, for example, ref [53])

$$\Omega_1(t + \Delta t, t) = \int_t^{t+\Delta t} d\tau_1 \, (-iH(\tau_1)) \tag{13a}$$

$$\Omega_2(t + \Delta t, t) = \frac{1}{2} \int_t^{t+\Delta t} d\tau_1 \int_t^{\tau_1} d\tau_2 \, [-iH(\tau_1), -iH(\tau_2)] \tag{13b}$$

$$\text{etc} \tag{13c}$$

From eq 12a,b and taking also into account that we can use the same method to integrate backward in time, we have that

$$y(t) = \exp(-\Omega(t + \Delta t, t))y(t + \Delta t) \tag{14a}$$

$$y(t) = \exp(\Omega(t, t + \Delta t))y(t + \Delta t) \tag{14b}$$

so $-\Omega(t + \Delta t, t) = \Omega(t, t + \Delta t)$. This implies that Ω does not contain even powers of Δt and it is immediately seen that

$$\Omega_1(t + \Delta t, t) = O(\Delta t) \qquad \Omega_2(t + \Delta t, t) = O(\Delta t^3) \tag{15a}$$

$$\Omega_{2s-1}(t + \Delta t, t) = O(\Delta t^{2s+1})$$
$$\Omega_{2s}(t + \Delta t, t) = O(\Delta t^{2s+1}), \quad s \geq 2 \tag{15b}$$

If we denote

$$\Omega^{[2]} = \Omega_1 \tag{16}$$

$$\Omega^{[2s]} = \sum_{k=1}^{2s-2} \Omega_k, \quad s \geq 2 \tag{1}$$

this implies that $\Omega^{[2s]} = \Omega + O(\Delta t^{2s+1})$, being an approximation of the order $2s$. In addition, in ref [68], it was proven that given a quadrature rule of the order, say $2s$, with nodes c_μ, $\mu = 1, ..., K$ and $\tau_\mu = t + c_\mu \Delta t$, the quantities $H(\tau_\mu)$ permit to approximate all nested integrals appearing in the Magnus series expansion up to the order $2s$.

For example, if we consider the Gauss−Legendre quadrature rules, one can get order $2s$ expressions with only s nodes, and we have

- Order two: $2s = 2$, $K = 1$, $c_1 = 1/2$, and

  $$\Omega_1 = -i\Delta t H(t + \Delta t/2) + O(\Delta t^3)$$

  so that

  $$y(t + \Delta t) = \exp(-i\Delta t H(t + \Delta t/2))y(t) \tag{17}$$

  is the exponential midpoint rule (EMR), of the second order in Δt.

- Order four: $2s = 4$, $K = 2$, $c_1 = (1/2) - \sqrt{3}/6$, $c_2 = (1/2) + \sqrt{3}/6$, and we can check that

  $$\Omega_1 + \Omega_2 = -i\frac{\Delta t}{2}(H(\tau_1) + H(\tau_2))$$
  $$- \frac{\sqrt{3}\,\Delta t^2}{12}[H(\tau_1), H(\tau_2)] + O(\Delta t^5)$$

  and then

  $$y(t + \Delta t) = \exp\left(-i\frac{\Delta t}{2}(H(\tau_1) + H(\tau_2))\right.$$
  $$\left. - \frac{\sqrt{3}\,\Delta t^2}{12}[H(\tau_1), H(\tau_2)]\right)y(t) \tag{18}$$

  is a fourth order approximation.

- Order six: $2s = 6$, $K = 3$, $c_1 = (1/2) - \sqrt{15}/10$, $c_2 = (1/2)$, $c_3 = (1/2) + \sqrt{15}/10$. For orders six and higher, it is convenient to work with graded algebras, as shown in ref [69] to simplify the enormous number of terms that will appear. For this purpose, one defines

  $$\hat{H}\left(\tau + t + \frac{\Delta t}{2}\right) = i\frac{1}{\Delta t}\left(\alpha_1 + \alpha_2 \frac{\tau}{\Delta t} + \alpha_3 \frac{\tau^2}{\Delta t^2}\right),$$
  $$\tau \in \left[-\frac{\Delta t}{2}, \frac{\Delta t}{2}\right],$$

  $$\alpha_1 = -i\Delta t H(\tau_2) = O(\Delta t),$$

  $$\alpha_2 = -i\Delta t \frac{\sqrt{15}}{3}(H(\tau_3) - H(\tau_1)) = O(\Delta t^2),$$

  $$\alpha_3 = -i\Delta t \frac{10}{3}(H(\tau_3) - 2H(\tau_2) + H(\tau_1)) = O(\Delta t^3) \tag{19}$$

This operator interpolates the Hamiltonian at the quadrature points: $\hat{H}(\tau_k) = H(\tau_k) \equiv H_k$, $k = 1, 2, 3$. The objects $\alpha_1, \alpha_2, \alpha_3$ can be considered as a graded algebra where $\alpha_1, \alpha_2, \alpha_3$ have grades 1, 2, and 3. Note that, for example, $[\alpha_j, [\alpha_k, \alpha_l]] = O(\Delta t^{j+k+l})$. In addition, given the equation

$$\dot{x}(t) = -i\hat{H}(t)x(t) \tag{20a}$$

$$x(0) = y_0 \tag{20b}$$

the following result is known (see 27 and references therein)

$$x(\Delta t) = y(\Delta t) + O(\Delta t^7)$$

so it suffices to solve the much simpler equation for $x(t)$ where $\hat{H}(t)$ is only a quadratic polynomial in t, and we can compute exactly the nested integrals in the Magnus series expansion. Notice that the qualitative properties of the solution are preserved since $\hat{H}(t)$ shares the same algebraic structure as $H(t)$. The relevant operators can now be written in terms of the $\alpha_1, \alpha_2, \alpha_3$ terms. For example

$$\Omega_1 = -i \int_t^{t+\Delta t} \hat{H}(\tau)\, d\tau = -i \int_{-\Delta t/2}^{\Delta t/2} \hat{H}$$

$$\left(\sigma + t + \frac{\Delta t}{2}\right) d\sigma = \alpha_1 + \frac{1}{12}\alpha_3$$

$$\Omega_2 = -\frac{1}{2} \int_t^{t+\Delta t} \int_t^{\sigma} [\hat{H}(\sigma), \hat{H}(\eta)]\, d\eta\, d\sigma$$

$$= -\frac{1}{12}[\alpha_1, \alpha_2] + \frac{1}{240}[\alpha_2, \alpha_3]$$

Including terms only up to the order six, we finally have

$$\Omega^{[6]} = \alpha_1 + \frac{1}{12}\alpha_3 - \frac{1}{12}[\alpha_1, \alpha_2] + \frac{1}{240}[\alpha_2, \alpha_3]$$
$$+ \frac{1}{360}[\alpha_1, [\alpha_1, \alpha_3]] - \frac{1}{240}[\alpha_2, [\alpha_1, \alpha_2]]$$
$$+ \frac{1}{720}[\alpha_1, [\alpha_1, [\alpha_1, \alpha_2]]] \tag{21}$$

Derived in a similar manner, methods up to the order 10 in this family can be found, for example, in ref 70.

Some gains in efficiency can be attempted if the Hamiltonian can be decomposed as

$$H(t) = T + V(t)$$

where T denotes the kinetic part and $V(t)$ is a time-dependent diagonal operator. From eq 19 and considering that $H(\tau_i) = T + V_i$ and therefore $H(\tau_i) - H(\tau_j) = V_i - V_j$, we have

$$\alpha_1 = -i\Delta t\, (T + V_2),$$

$$\alpha_2 = -i\Delta t \frac{\sqrt{15}}{3}(V_3 - V_1),$$

$$\alpha_3 = -i\Delta t \frac{10}{3}(V_3 - 2V_2 + V_1) \tag{22}$$

so that the element $[\alpha_2, \alpha_3]$ vanishes and

$$[\alpha_2, [\alpha_1, \alpha_2]] = \frac{5\Delta t^3}{3} \|\nabla V_3 - \nabla V_1\|^2$$

where ∇V_k, $k = 1, 3$ denote the gradient of the potential evaluated at τ_k. Notice that it is a diagonal operator and commutes with α_2 and α_3.

The EMR is not only the simplest but also an exception among the Magnus integrators, as their evaluation in all other cases involve the computation of Hamiltonian commutators, a computationally expensive procedure. To avoid this problem, one may look for commutator-free approximations to the Magnus expansions.[62,71,72] In general, they are given by products of exponentials such as

$$y(t + \Delta t) = \Gamma_M^{[2s]}(H) y(t) \tag{23a}$$

$$\Gamma_M^{[2s]}(H) = \prod_{k=1}^{M} \exp\left[\sum_{l=1}^{s} x_{kl}\alpha_l\right]$$
$$= \prod_{k=1}^{M} \exp\left[-i\Delta t \sum_{\mu}^{K} \gamma_{k\mu} H(\tau_\mu)\right] \tag{23b}$$

which agree with the exact solution up to a desired order. M is the number of exponentials of the method, $2s$ is the accuracy order of the resulting method and the x_{kl} and $\gamma_{k\mu}$ coefficients are some properly chosen coefficients. If the Gauss−Legendre quadrature rule is used, then $K = s$. The lowest order of all of these methods is in fact also the EMR, which is second order and requires only one exponential: EMR = $\Gamma_1^{[2]}$.

To apply these formulas, one needs the Hamiltonian at K times $\{\tau_\mu\}$ within the propagating interval $[t, t + \Delta t]$. In principle, one could think of applying these propagators also for the nonlinear case, making the identification

$$H(\tau_\mu) \equiv H(y(\tau_\mu), \tau_\mu) \tag{24}$$

However, the difficulty lies in the fact that the states $y(\tau_\mu)$ for $t < \tau_\mu \leq t + \Delta t$ are unknown and therefore also the Hamiltonians $H(\tau_\mu)$ are unknown. In this work, we address this problem by employing the extended variables concept described previously (eq 7a,b). The approximated solution $u(t)$ can be obtained via an extrapolation or interpolation formula, making use of the solution at previous time steps. Alternatively, one may directly extrapolate the Hamiltonian; $H(\tau_\mu)$ can be obtained through some interpolation or extrapolation formula, i.e., making use of a series of Hamiltonians at several time steps. We will use the notation $H[\tau_\mu]$ for the resulting approximation, as opposed to $H(\tau_\mu)$ for the exact Hamiltonian. There are two options

- One may write $H[t_\mu]$ as an interpolated approximation that makes use of the "future" $H(t + \Delta t)$, in addition to a number of the "past" Hamiltonians

$$H[\tau_k] = \text{Interp}[H(t + \Delta t), H(t), H(t - \Delta),$$
$$H(t - 2\Delta t), ..., H(t - m\Delta t)] \tag{25}$$

  We call it an interpolation because τ_k belongs to the interval covered by the used Hamiltonians. Since $H(t + \Delta t)$ is also unknown, the resulting propagator formula is an implicit equation that has to be solved for $y(t + \Delta t)$.

- One may also write $H[t_\mu]$ as an extrapolated approximation that does not make use of the unknown $H(t + \Delta t)$

$$H[\tau_k] = \text{Extrap}[H(t), H(t-\Delta), H(t-2\Delta t),$$
$$..., H(t-m\Delta t)] \tag{26}$$

  The resulting formula is an explicit transformation of $y(t)$ into $y(t + \Delta t)$. Due to this simplicity, we will only use this choice hereafter.

To perform the extrapolation, one must store the state at previous time steps $y(t - \Delta t), ..., y(t - m\Delta t)$ (or the corresponding Hamiltonians, whatever is more convenient). If the underlying linear method is of mth order, the extrapolation must be of $(m - 1)$th order (or higher). In this way, the resulting scheme is mth order also for nonlinear systems.

The block-diagonal structure of our target eq 9 permits to treat the two subsystems separately

$$\begin{pmatrix} q(t + \Delta t) \\ v(t + \Delta t) \end{pmatrix} = \Gamma_M^{[s]}(H_C) \begin{pmatrix} q(t) \\ v(t) \end{pmatrix} \qquad (27)$$

$$\varphi(t + \Delta t) = \Gamma_M^{[s]}(H_{KS}) \varphi(t) \qquad (28)$$

We have implemented four versions of the CFM, two order four propagators and two of order six. In all cases, the final algorithm for the propagation is

1. Compute $\{q[t_\mu]\}$ extrapolating from $q(t)$, $q(t - \Delta t)$, ..., $q(t - m\Delta t)$. Although the use of extrapolation apparently does away with the symplecticity of the method, $q(t + \Delta t)$ is calculated through the exponential of a symplectic matrix, and the symplecticity of the system is preserved.

2. Compute $\{F[t_\mu]\}$ extrapolating from $F(t)$, $F(t - \Delta t)$, ..., $F(t - m\Delta t)$.

3. Compute $\{H_{KS}[t_\mu]\}$, extrapolating from $H_{KS}(t)$, $H_{KS}(t - \Delta t)$, ..., $H_{KS}(t - m\Delta t)$.

4. $H_C[t_\mu] = i \begin{pmatrix} 0 & 1 \\ \dfrac{1}{m} \dfrac{F[t_\mu]}{q[t_\mu]} & 0 \end{pmatrix}$

5. $\begin{pmatrix} q(t + \Delta t) \\ v(t + \Delta t) \end{pmatrix} = \Gamma_M^{[s]}(H_C) \begin{pmatrix} q(t) \\ v(t) \end{pmatrix}$

6. $\varphi(t + \Delta t) = \Gamma_M^{[s]}(H_{KS}) \varphi(t)$

7. Compute $F(t + \Delta t)$ and $H_{KS}(t + \Delta t)$, necessary inputs for the next iteration.

We briefly describe now the four CF formulas that we have implemented and benchmarked (in addition to the EMR described above).

2.2.1. $\Gamma_2^{[4]}$. The first fourth order method that we have implemented is composed of two exponentials[62,72−74] and is defined by

$$\Gamma_2^{[4]}(H) = \exp\{-i\Delta t(a_{11}H[t_1] + a_{12}H[t_2])\}$$
$$\times \exp\{-i\Delta t(a_{12}H[t_1] + a_{11}H[t_2])\} \qquad (29)$$

where the constants a_{ij} and t_i are given by

$$\begin{cases} a_{11} = \dfrac{3 - 2\sqrt{3}}{12}, & a_{12} = \dfrac{3 + 2\sqrt{3}}{12} \\[2mm] c_1 = \dfrac{1}{2} - \dfrac{\sqrt{3}}{6}, & c_2 = \dfrac{1}{2} + \dfrac{\sqrt{3}}{6} \\[2mm] t_1 = t + c_1\Delta t, & t_2 = t + c_2\Delta t \end{cases} \qquad (30)$$

2.2.2. $\Gamma_4^{[4]}$. We have tried another fourth-order method, $\Gamma_4^{[4]}$.[63] It is designed for Hamiltonian functions that can be decomposed into two parts

$$H(y(t), t) = T + V(y(t), t) \qquad (31)$$

The first part, the "kinetic" term T, is linear and time independent, whereas the second one, the "potential" term $V(y(t), t)$ is not, but its exponential is easy to calculate (for example, because it is diagonal). The scheme is given by

$$\Gamma_4^{[4]} = \exp\{-i\Delta t \tilde{V}_4\}\exp\{-i\frac{\Delta t}{2}(T + \tilde{V}_3)\}$$
$$\times \exp\{-i\frac{\Delta t}{2}(T + \tilde{V}_2)\}\exp\{-i\Delta t \tilde{V}_1\}$$

where

$$\begin{cases} \tilde{V}_1 = a_{11}V_1 + a_{12}V_2 + a_{13}V_3 \\ \tilde{V}_2 = a_{21}V_1 + a_{22}V_2 + a_{23}V_3 \\ \tilde{V}_3 = a_{23}V_1 + a_{22}V_2 + a_{21}V_3 \\ \tilde{V}_4 = a_{13}V_1 + a_{12}V_2 + a_{11}V_3 \end{cases} \qquad (32)$$

and

$$V_1 = V[t + c_1\Delta t], \quad V_2 = V[t + c_2\Delta t], \quad V_3 = V[t + c_3\Delta t] \qquad (33)$$

are extrapolated potentials. The idea is to profit from a fast evaluation of the two exponentials of the potentials, exp-$\{-i\Delta t \tilde{V}_1\}$ and $\exp\{-i\Delta t \tilde{V}_4\}$, so that in practice, the cost is similar to that of a method with only two exponentials.

The constants that appear in these equations are given by

$$\begin{cases} a_{11} = \dfrac{10 + \sqrt{15}}{180}, & a_{12} = -\dfrac{1}{9}, & a_{13} = \dfrac{10 - \sqrt{15}}{180} \\[2mm] a_{21} = \dfrac{15 + 8\sqrt{15}}{90}, & a_{22} = \dfrac{2}{3}, & a_{23} = \dfrac{15 - 8\sqrt{15}}{90} \\[2mm] c_1 = \dfrac{1}{2} - \dfrac{\sqrt{15}}{10}, & c_2 = \dfrac{1}{2}, & c_3 = \dfrac{1}{2} + \dfrac{\sqrt{15}}{10} \end{cases} \qquad (34)$$

The method uses a sixth-order quadrature rule but is only fourth order in Δt because it has just five parameters to solve six independent order conditions. It can however be considered as an optimized fourth-order scheme, as long as the commutation relation $[\alpha_2, \alpha_3] = 0$ is fulfilled, given the generators defined in eq 22.

In our case, the division of the Hamiltonian must be done for both the quantum and the classical subsystems

$$H(y(t), t) = \begin{pmatrix} H_C(q(t), \varphi(t), t) & 0 \\ 0 & H_{KS}(q(t), \varphi(t), t) \end{pmatrix}$$
$$= \begin{pmatrix} T_C + V_C(q(t), \varphi(t), t) & 0 \\ 0 & T_Q + V_Q(q(t), \varphi(t), t) \end{pmatrix} \qquad (35)$$

Likewise, one may define the corresponding classical and quantum generators α_{Ci} and α_{Qi}, respectively, which must verify the commutation rules.

For the quantum part, the division is obvious, as we do have natural "kinetic" and "potential" terms. The commutator relation $[\alpha_{Q2}, \alpha_{Q3}] = 0$ is fulfilled, as it only involves potential terms that are diagonal in real space and therefore commute with each other. For the classical Hamiltonian, eq 10, we have

$$\alpha_{C1} = \begin{pmatrix} 0 & 1 \\ \hat{\alpha}_{C1} & 0 \end{pmatrix}, \quad \alpha_{Ck} = \begin{pmatrix} 0 & 0 \\ \hat{\alpha}_{Ck} & 0 \end{pmatrix}, \quad k = 2, 3$$

with $\hat{\alpha}_{C1} = \Delta t \dfrac{1}{m} \dfrac{F[\tau_2]}{q[\tau_2]}$, $\hat{\alpha}_{C2} = \Delta t \dfrac{\sqrt{15}}{3m} \left(\dfrac{F[\tau_3]}{q[\tau_3]} - \dfrac{F[\tau_1]}{q[\tau_1]} \right)$, ..., and the commutator relation $[\alpha_{C2}, \alpha_{C3}] = 0$ is also fulfilled. In addition,

the matrix associated to $[\alpha_{C2}, [\alpha_{C1}, \alpha_{C2}]]$ has the same simple structure as α_{C2} and α_{C3}.

2.2.3. $\Gamma_5^{[6]}$. The first order 6 method that we have implemented ($\Gamma_5^{[6]}$) requires five exponentials, but using the same division of the Hamiltonian into a kinetic and a potential term described for $\Gamma_4^{[4]}$, only three of those are costly, whereas two of them are potential exponentials

$$\Gamma_5^{[6]} = \exp\{-i\Delta t\tilde{V}_5\}\exp\{-i\Delta t(b_1 T + \tilde{V}_4)\}$$
$$\times \exp\{-i\Delta t(b_2 T + \tilde{V}_3)\}\exp\{-i\Delta t(b_1 T + \tilde{V}_2)\}\exp\{-i\Delta t\tilde{V}_1\}$$

The potential terms $\tilde{V}_i$ are linear combinations of V_1, V_2, and V_3, which are defined in eq 33. The quadrature points c_i are the same as in $\Gamma_4^{[4]}$, given in eq 34.

2.2.4. $\Gamma_4^{[6]}$. We have also tested a second order-six method, ($\Gamma_4^{[6]}$), which only involves four exponentials, two of which only have potential terms[63,75]

$$\Gamma_4^{[6]} = \exp\{-i\Delta t(\tilde{V}_4 + \Delta t^2\tilde{V})\}\exp\{-i\Delta t/2(T + \tilde{V}_3)\}$$
$$\times \exp\{-i\Delta t/2(T + \tilde{V}_2)\}\exp\{-i\Delta t(\tilde{V}_1 + \Delta t^2\tilde{V})\} \quad (36)$$

Once again, the potential terms $\tilde{V}_i$ are linear combinations of V_1, V_2, and V_3. The novelty is the presence of the term $\tilde{V}$, given by

$$\tilde{V} = i\frac{y}{\Delta t^3}[\alpha_2, [\alpha_1, \alpha_2]] \quad (37)$$

where $y = 1/43\,200$ and α_i are the generators defined in eq 22.

The presence of these commutator terms contradicts the "commutator-free" character of the methods that we are advocating. However, in some circumstances it may be advantageous to include some commutators if they are easy to compute, as we shall see below. This is of course problem— and implementation—dependent. As in previous cases, the classical and quantum parts can be treated separately.

- Regarding the quantum part, the commutators defining $\tilde{V}_Q$

$$\tilde{V}_Q = i\frac{y}{\Delta t^3}[\alpha_{Q2}, [\alpha_{Q1}, \alpha_{Q2}]] \quad (38)$$

can then be worked out assuming that the potential term is a local function in real space. The result is

$$\tilde{V}_Q = -\frac{1}{25\,900}\left\|\nabla V_{Q3} - \nabla V_{Q1}\right\|^2 \quad (39)$$

For the efficiency of the method, it is important that this term can be easily computed. If it is neglected or not computed exactly, then the method order is reduced to four. However, the fourth-order error term prefactor may be very small and the method may appear as sixth order until very high accuracies.

- For the nuclear case, the equation reads

$$\begin{pmatrix} q(t + \Delta t) \\ v(t + \Delta t) \end{pmatrix} = \exp\{-i\Delta t(\tilde{H}_{C4} + \Delta t^2\tilde{H}_C)\}$$
$$\times \exp\{-i\Delta t/2\tilde{H}_{C3}\}\exp\{-i\Delta t/2\tilde{H}_{C2}\}$$
$$\times \exp\{-i\Delta t(\tilde{H}_{C1} + \Delta t^2\tilde{H}_C)\}\begin{pmatrix} q(t) \\ v(t) \end{pmatrix} \quad (40)$$

The $\tilde{H}_{Cj}$ matrices are linear combinations of H_{Cj}

$$H_{Cj} = H_C[t_j] = i\begin{pmatrix} 0 & \delta_{j2} + \delta_{j3} \\ \lambda_j & 0 \end{pmatrix} \quad (41)$$

for $\lambda_j = ((1)/(m))F[t_j]/q[t_j]$. The extra term $\tilde{H}_C$ must be computed by considering its definition as a nested commutator, yielding

$$\tilde{H}_C = i\frac{y}{\Delta t^3}[\alpha_{C2}, [\alpha_{C1}, \alpha_{C2}]]$$
$$= \frac{i}{51\,840}\begin{pmatrix} 0 & 0 \\ (\lambda_3 - \lambda_1)^2 & 0 \end{pmatrix} \quad (42)$$

3. RESULTS

We have analyzed the performance of these CFM methods for hybrid systems, by simulating molecules in the presence of a laser field. We have used the hydrogen molecule as the base for our benchmarks, since it is one of the simplest, but we have also tried some tests with the benzene molecule, to see how the methodology may scale to larger systems. The methods have been implemented in the octopus code,[64,65] a real-space pseudo-potential code that permits to perform Ehrenfest-TDDFT simulations. Regarding numerical details, the molecule was placed in a spherical simulation box of radius $R = 10$ au, containing a regular rectangular grid with a spacing of $h = 0.4$ au. The total simulation time was set to $T = 20\pi$ au. The molecule was subject to the effect of a laser pulse $e(t)$ with the shape

$$e(t) = A\sin(\omega t) \quad (43)$$

where the amplitude was set to $A = 0.1$ au and the frequency to $\omega = 10$ au.

To study the accuracy of the propagators, we compared the wave function at the end of the propagation with a reference "exact" calculation, obtained using the standard explicit fourth-order Runge–Kutta propagator with a much smaller time step. We defined the error in the wavefunction as

$$E_{wf} = \sqrt{\sum_m \|\varphi_m(T) - \varphi_m^{exact}(T)\|^2} \quad (44)$$

where φ_m^{exact} are the reference KS orbitals from the "exact" computation. Since we are not only interested in the accuracy but also on the performance of the propagators, we measured the cost of the propagator in wall-time seconds for a full run of the simulation. The cost was plotted as a function of the wave function error previously defined.

Figures 1–4 summarize the results of the simulations for the EMR and the four CFM methods described above, when applied to the hydrogen molecule. In addition, for the sake of comparison, the plots also display results obtained with the explicit fourth order Runge–Kutta (RK4). Notice that 1 au of time equals 24 attoseconds (as), approximately. Therefore, for example $\log_{10}(\Delta t) = -2$ corresponds to 0.24 as. The first two figures, Figures 1 and 2, display the results of calculations for which the extrapolation was done at the same order of accuracy than the underlying method, i.e., 2 for the EMR, 4 for $\Gamma_2^{[4]}$ and $\Gamma_4^{[4]}$, and 6 for $\Gamma_5^{[6]}$ and $\Gamma_4^{[6]}$. For the last two, Figures 3 and 4, the extrapolation was done at a much higher order (12).

Figure 1 displays the error in the wave function as a function of the time step. Using logarithmic scales on both axes, the curves are (approximately) straight lines whose slope reveals
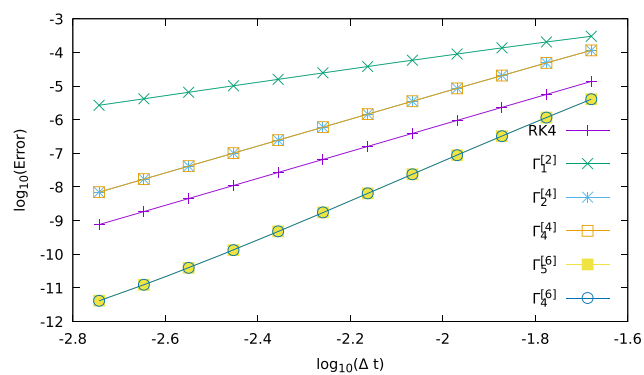
Figure 1. [Hydrogen molecule] Error in the propagation, measured as the difference of the propagated KS orbital with respect to the quasi-exact one (computed with a tiny time step), as a function of the time step. Both the error and the time step are shown in a logarithmic scale. The extrapolation is done at the same order of the underlying method.
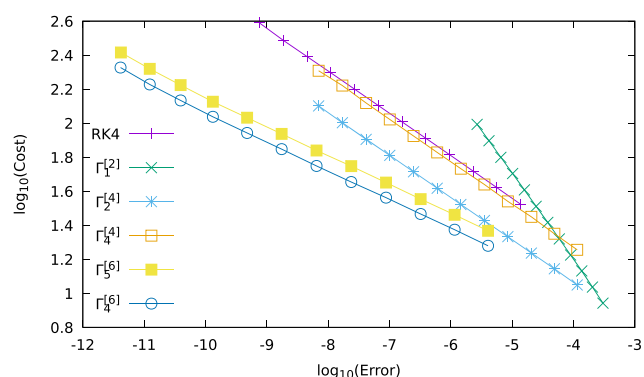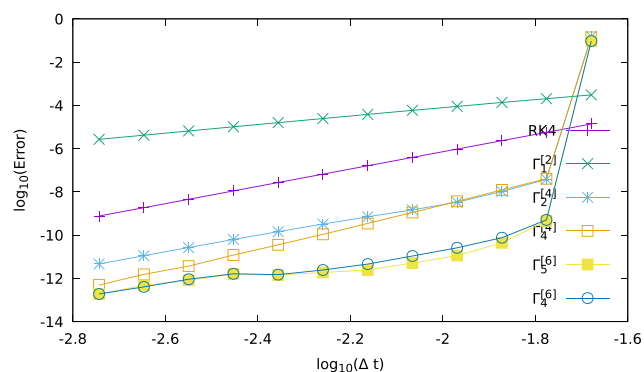

Figure 2. [Hydrogen molecule] Cost in seconds (scale in left axis), as a function of the error. The extrapolation is done at the same order of the underlying method.

Figure 3. [Hydrogen molecule] Error in the propagation, measured as the difference of the propagated KS orbital with respect to the quasi-exact one (computed with a tiny time step), as a function of the time step. Both the error and the time step are shown in a logarithmic scale. The extrapolation is done at order 12.

Figure 4. [Hydrogen molecule] Cost in seconds (scale in left axis) as a function of the error. The extrapolation is done at order 12.

the accuracy order of the propagator. We can see that the CFM integrators are significantly more precise than the EMR, with a difference that grows as the value of Δt is reduced. In this figure, the CFM methods of a given order are indistinguishable, as they produce results with almost equal accuracy. The reason, as we shall see, is that the error in this case is dominated by the extrapolation error, which is the same for
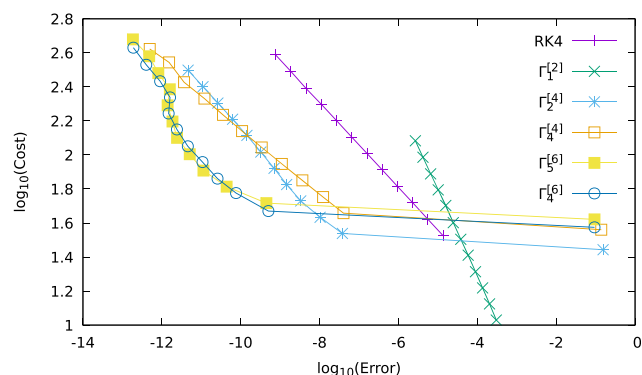
methods of equal order. At any given time step, the RK4 scheme is more precise than the order four CFM integrators.

In Figure 2, we present the cost (in seconds) of the propagation, as a function of the error in the wave function, for the same runs presented in the previous figure. The axes are again in a logarithmic scale. This cost is of course dependent on the system and the hardware used for the simulation, although the results given here may serve as a qualitative indicator of the performance of the integrators. These cost vs accuracy plots permit to identify the most efficient methods for a given required accuracy. Not all applications demand the same level of accuracy, and the efficiency of the methods depends on it. As a rule of thumb, the more sophisticated propagators perform better when very stringent accuracies are needed and simpler propagators become more useful if the needed precision is not that high. This is indeed the conclusion that can be drawn from Figure 2.

The results obtained with extrapolations done at a higher order (12), shown in Figures 3 and 4, have a much better accuracy, except for the results of the EMR, which are similar. One may conclude from this fact that the dominant error in the previous cases was due to the extrapolation. This error is not present now, as we have increased the extrapolation error to the limit in which it is converged. The two order four methods almost reach numerical accuracy ($\approx 10^{-12}$) at around $\log_{10}(\Delta t) \approx -2.8$; the method that requires four exponentials, $\Gamma_4^{[4]}$ is slightly more accurate, and in fact its order (the slope of the curve in the region where it is approximately its straight line) is higher than 4. $\Gamma_2^{[4]}$, in contrast, shows its predicted fourth order behavior. Both these order four CFM methods, when using higher-order extrapolations, become more accurate than the RK4 integrator.

The two order six methods behave similarly, and already reach numerical accuracy at a much larger time step. On the negative side, however, the first data point on the plot for all order 4 and 6 methods, corresponding to the larger time step ($\log_{10}(\Delta t) \approx -1.7$, on the right side) has a large error, which corresponds to the onset of instability: larger time steps quickly lead to exponentially growing errors. This is due to the inherent error of high-order extrapolation formulas. Therefore, although this high-order extrapolation permits to increase the accuracy (in fact, by several orders of magnitude), it has the side effect of reducing the stability region.

Figure 4 presents the cost vs accuracy results for the same computations: it may be seen how the selection of the optimal method depends on the required accuracy: if one needs very precise calculations, the order six methods perform best; on

the contrary, if low accuracies suffice, it may occur that the instability alluded before may imply the need to use the EMR. For intermediate situations, the order four methods would be the best option.

The hydrogen molecule used to perform these benchmarks was deliberately chosen to be small to permit fast extensive testing. However, one should assess whether the main conclusions translate to larger systems. Therefore, in Figures 5 and 6 we display similar results but for calculations
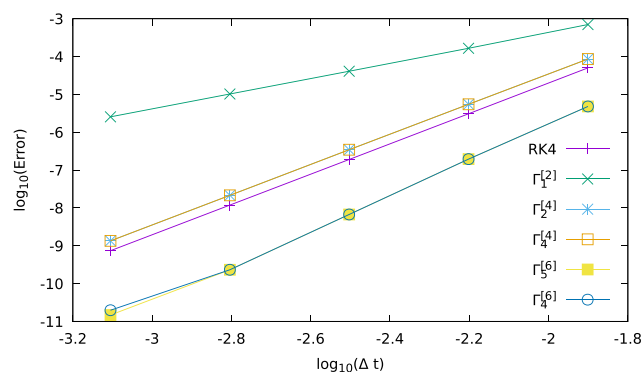

Figure 5. [Benzene molecule] Error in the propagation, measured as the difference of the propagated KS orbital with respect to the quasi-exact one (computed with a tiny time step), as a function of the time step. Both the error and the time step are shown in a logarithmic scale. The extrapolation is done at the same order of the underlying method.
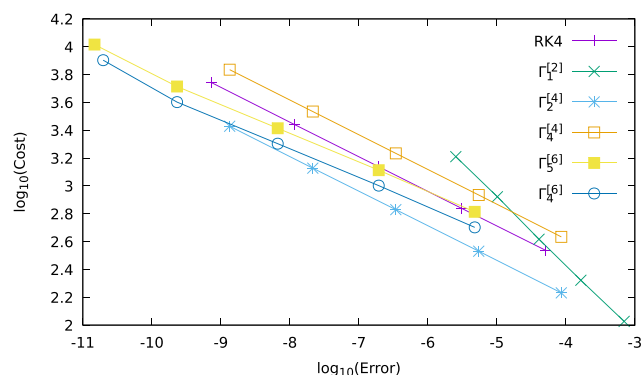

Figure 6. [Benzene molecule] Cost in seconds (scale in left axis) as a function of the error. The extrapolation is done at the same order of the underlying method.

performed on the benzene molecule. Instead of two nuclei and two electrons, it has 12 nuclei and 30 valence electrons (the core electrons are handled through the use of pseudopotentials). The qualitative behavior of the methods is not affected by system size, as it can be deduced from these figures. However, the threshold precision for which the higher order methods become more cost effective than the lower order ones is of course problem dependent.

Finally, we note that the results shown in all previous figures correspond to serial calculations. The octopus code, however, admits various parallelization schemes, and any of these algorithms can make use of them. One may then wonder how the various schemes differ regarding the scalability with the number of nodes. In this respect, we have observed no significant differences. There are two possible parallelization procedures: separating pieces of each molecular orbital into the

various nodes, dividing the real space into domains, or placing different orbitals into various nodes (if the system has several orbitals). Both procedures can be used simultaneously. The propagators described in this work essentially require two kinds of operations that use most of the time: (1) application of the Hamiltonian to a given orbital; (2) construction of the nonlinear Hamiltonian from a given orbital set. The first step requires communication among nodes when the first parallelization scheme is used, whereas the second step requires communication among nodes when the second scheme is used. However, all methods described here have similar requirements and we could see no clear advantage of any of the schemes regarding the possible scalability. Of course, for very large systems, the situation could change, and more careful benchmarking should be done.

4. CONCLUSIONS

We have studied a family of methods to propagate quantum-classical hybrid systems (quantum electrons, classical nuclei): the (quasi)-commutator-free Magnus expansions. In particular, we have chosen two order four and two order six expansions, in addition to the exponential midpoint rule, which can be considered as an order two member of this family. For the quantum part, we have employed time-dependent density-functional theory to handle the many-electron problem, although the methods described here can be directly applied for any other time-dependent electronic structure theory.

Instead of using different and independent propagators for the classical and quantum parts, we have rewritten the full dynamics as a nonlinear Schrödinger-like equation. Then, we may apply the same propagator for both the classical and quantum parts of the system. We have employed, however, a family of schemes, the commutator-free Magnus expansions, which was developed for linear systems. The formulas for propagating the system at a given time step requires the application of the Hamiltonian at intermediate instants of the step, and for nonlinear Schrödinger equations this Hamiltonian is unknown. We have circumvented this problem by performing an extrapolation from previous time steps. This extrapolation must be done at least at the same order of accuracy as the underlying method to preserve it; however, we have observed how it is convenient to go beyond this order, as one can significantly increase the accuracy by doing so.

The use of an algorithm designed from the start for the combined system permits to ensure its properties (i.e., preservation of the symplectic structure, accuracy order with respect to the time step), whereas using a different algorithm for each system does not. For example, the Verlet algorithm is second order in Δt, and its use in combination with any method would lead to an overall method of order two at most. In addition, our numerical tests prove that the proposed schemes are computationally efficient. The choice of method, however, depends on the required accuracy: if very precise calculations are required, it is better to choose a higher order Magnus expansion, such as any of the two sixth-order expansions that we have tested. For lower accuracies, the fourth-order schemes may suffice and are better than the simplest of the Magnus expansions, the exponential midpoint rule. In addition, if lower accuracies suffice, the higher-order formulas may become unstable at larger time steps.

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Notes

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