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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 equations geometrical structure. 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 non-linear: formally, the full quantum-classical system can be rewritten as a non-linear Schrodinger equation, i.e. one in which the Hamiltonian depends on the system itself. The Magnus expansions algorithms for linear systems require the application of the Hamiltonian at intermediate points in a given propagating interval. For non-linear 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 multi-step technique or, alternatively, as a predictor corrector formula.

1 Introduction

Molecular Dynamics[1] (MD) has become a well established field since its inception in the 50's.[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 *non-adiabatic* version of MD, and the dynamical problem may then be *hybrid*, mixing both classical and quantum degrees of freedom that evolve simultaneously and coupled to each other. In this paper we focus on the propagation of these hybrid quantum-classical systems.[4,5]

The two different particle types implies 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[6] 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.[7–9] for a general introduction, and make a quick summary here (some of the following ideas have been tested in combination with TDDFT[10–21]):

- 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 multi-step (that use information from a number of previuos time steps). The latter ones have only recently been explored in this context of electronic wave function dynamics.[13,22]

- The Runge-Kutta (RK) family is the most successful family of general purpose single step integrators.[23] Also, numerous variations exist: partitioned RK, embedded formulas, extrapolation methods (e.g. the Gragg-Bulirsch-Stoer algorithm[24]), composition techniques, the linearly implicit Rosenbrock methods, etc.

- One may also make use of the linear structure of 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,[25] with the Chebychev[26] and Krylov polynomial expansions,,[27,28] with Leja and Padé interpolations,[29] etc. These ideas may be extended to non-autonomous, or even non-linear Hamiltonians.[30]

- 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[31] or Strang[32] splittings), such as with the split operator formula,[33] or with more sophisticated formulas.[34–37]

- If the Hamiltonian contains a linear term (e.g. the kinetic operator) and a non-linear 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[13,38,39] or the exponential integrators[40–43] (exponential Runge-Kutta, integrating factor, exponential time-differencing, etc.).

- Working on a adiabatic or spectral basis, in various similar manners,[12,14,44–47] 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[48] that it could be substituted by the normal exponential of a different operator, that can be given as a series expansion.[49] This idea has led to a family of techniques, the *Magnus expansions*, that 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 in order to assure that the properties of the propagator (symplecticity, time reversal symmetry, stability, order of accuracy...) are conserved. However, few authors have considered the design of specifically hybrid propagators.[50–57]

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 non-linear Schrödinger-like form, and together with the Kohn-Sham equations we use the recently developed commutator-free Magnus expansions[58,59] (CFM) to propagate the whole system. In a previous work,[22] we found that, in the context of TDDFT, a fourth order implementation of these integrators has an outstanding performance compared to other well stablished integrators such as the exponential midpoint rule or the classical fourth order Runge-Kutta propagator. This has been the motivation to extend the previous study to (1) study to 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 non-linear, the former through the Hamiltonian dependence on the electronic density. The resulting hybrid model is therefore also non-linear, and can be formulated as a non-linear 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 non-linear 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 non-linear 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 multi-step explicit propagator, and implies the need to save a number of previos 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 implemeted these propagation schemes in the octopus[60,61] 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 non-adiabatic 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 non-interacting one, that nevertheless has the same density – an object from which in principle (not always in practice) any observable can be extracted. The fictitious non-interacing 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:

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

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 non-linear Schrödinger-like equations that depend on a density-dependent potential whose precise form has to be approximated. When coupled with the clasical nuclei, the resulting Ehrenfest-TDDFT model is:

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

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

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

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 $\hat{H}_{\mathrm{KS}}(q,\varphi)$ is the Kohn-Sham Hamiltonian (that typically depends on the position, but not the momenta, of the nuclei, and which depends also on the KS orbitals φ through their density). These last two objects are given by:

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

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

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[62]) 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 non-linear equations because the KS Hamiltonian depends on the electronic density, which in turn depends on the KS orbitals. In any case, the resulting model, Eqs. (3), is nonlinear, even in the absence of that TDDFT nonlinearity [i.e. Eqs. (1)], 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 may also destroy some of the properties that are expected from any of the two methods: the order of accuracy with respect to the time-step, the preservation of the symplectic structure, etc.

There have been various proposals for schemes that truly approach the combined system.[50–57] 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.[4,63] 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, in order 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 non-linear

Schrödinger equation, i.e.:

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

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

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

$$y = \begin{bmatrix} q \\ v \\ \varphi \end{bmatrix} \tag{7}$$

Here, we are using as a shorthand notation q for all the nuclear position coordinates, v for all their velocities, and φ for all the KS orbitals coefficients in some basis or representation. The non-linear Schrödinger equation may then be written as:

$$\begin{pmatrix} \dot{q}(t) \\ \dot{v}(t) \\ \dot{\varphi}(t) \end{pmatrix} = -i \begin{pmatrix} H_C(q(t),\varphi(t),t) & 0 \\ 0 & H_{\mathrm{KS}}(q(t),\varphi(t),t) \end{pmatrix} \begin{pmatrix} q(t) \\ v(t) \\ \varphi(t) \end{pmatrix}. \tag{8}$$

The "classical" Hamiltonian matrix H_C is:

$$H_C(q(t),\varphi(t),t) = i \begin{pmatrix} 0 & 1 \\ \frac{F(q(t),\varphi(t),t)}{mq(t)} & 0 \end{pmatrix}. \tag{9}$$

Note that in order to render the classical equations into "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 non-autonomous linear system,

$$\dot{y}(t) = -iH(t)y(t)\,, \tag{10a}$$

$$y(0) = y_0\,. \tag{10b}$$

the solution is given, in a neighbourhood of t, as:

$$y(t+\Delta t) = \exp(\Omega(t+\Delta t, t))y(t), \tag{11a}$$

$$\Omega(t+\Delta t, t) = \sum_{k=1}^{\infty} \Omega_k(t+\Delta t, t)\,. \tag{11b}$$

This is the Magnus expansion.[48] The Ω_k terms are defined in terms of multivariate integrals of nested commutators of increasing order (see for example Ref. 49):

$$\Omega_1(t+\Delta t, t) = \int_t^{t+\Delta t} \mathrm{d}\tau_1 (-iH(\tau_1))\,, \tag{12a}$$

$$\Omega_2(t+\Delta t, t) = \frac{1}{2}\int_t^{t+\Delta t} \mathrm{d}\tau_1 \int_t^{t+\Delta t} \mathrm{d}\tau_1 \left[-iH(\tau_1), -iH(\tau_2)\right]\,. \tag{12b}$$

$$\text{etc.} \tag{12c}$$

When the series is truncated at order k, the resulting algorithm is accurate to order $2k$ in Δt – as long as the Ω_k are integrated with quadratures of that order.

For example, the exponential midpoint rule (EMR), the result of truncating Eqs. (11) at $k = 1$, is second order in Δt:

$$y(t+\Delta t) = \exp(-i\Delta t H(t+\Delta t/2))y(t)\,. \tag{13}$$

The EMR is the simplest, and an exception among the Magnus integrators, as their evaluation in all other cases involve the computation of Hamiltonian commutators, a computationally expensive procedure.

In order to avoid this problem, one may look for commutator-free approximations to the Magnus expansions.[58] In general, they are given by products of exponentials such as:

$$y(t+\Delta t) = \Gamma_M^{[S]}(H) y(t), \tag{14a}$$

$$\Gamma_M^{[S]}(H) = \prod_{k=1}^{M} \exp\left[-i\Delta t \sum_{\mu}^{K} \alpha_{k\mu} H(\tau_\mu) \right], \tag{14b}$$

where M is the number of exponentials of the method and S is the accuracy order of the resulting method. One needs the Hamiltonian at K times τ_μ, within the propagating interval $[t, t+\Delta t]$. In principle, one could think of applying these propagators also for the non-linear case, making the identification:

$$H(\tau_\mu) \equiv H(y(\tau_\mu), \tau_\mu)\,. \tag{15}$$

However, the difficulty is 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. This problem can be solved by approximating $H(\tau_\mu)$ 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 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:

  $$H[\tau_k] = \text{Interp}[H(t+\Delta t), H(t), H(t-\Delta), H(t-2\Delta t), \dots, H(t-s\Delta t)]. \tag{16}$$

  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 $H(t+\Delta t)$:

$$H[\tau_k] = \mathrm{Extrap}[H(t), H(t-\Delta), H(t-2\Delta t), \ldots, H(t-s\Delta t)]. \tag{17}$$

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

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

The block-diagonal structure of our target Eq. (8) permits to treat the two subsystems separately:

$$\begin{pmatrix} q(t+\Delta t) \\ v(t+\Delta t) \end{pmatrix} = \Gamma_M^{[S]}(H_C) \begin{pmatrix} q(t) \\ v(t) \end{pmatrix}, \tag{18}$$

$$\varphi(t+\Delta t) = \Gamma_M^{[S]}(H_{\mathrm{KS}})\varphi(t)\,. \tag{19}$$

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 $q(t), q(t-\Delta t), \ldots, q(t-s\Delta t)$.
2. Compute $\{F[t_\mu]\}$ extrapolating from $F(t), F(t-\Delta t), \ldots, F(t-s\Delta t)$.
3. Compute $\{H_{\mathrm{KS}}[t_\mu]\}$, extrapolating from $H_{\mathrm{KS}}(t), H_{\mathrm{KS}}(t-\Delta t), \ldots, H_{\mathrm{KS}}(t-s\Delta t)$.
4. $H_C[t_\mu] = i \begin{pmatrix} 0 & 1 \\ \frac{1}{m}\frac{F[t_\mu]}{q[t_\mu]} & 0 \end{pmatrix}$
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. $\varphi(t+\Delta t) = \Gamma_M^{[S]}(H_{\mathrm{KS}})\varphi(t)$

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

2.2.1 $\Gamma_2^{[4]}$

The first 4th order method that we have implemented is composed of two exponentials,[58,64] and is defined by:

$$\Gamma_2^{[4]}(H) = \exp\{-i\Delta t(\alpha_1 H[t_1] + \alpha_2 H[t_2])\} \exp\{-i\Delta t(\alpha_2 H[t_1] + \alpha_1 H[t_2])\}\,, \tag{20}$$

where the constants α_i and t_i are given by:

$$\begin{cases} \alpha_1 = & \dfrac{3-2\sqrt{3}}{12}, \qquad \alpha_2 = \dfrac{3+2\sqrt{3}}{12}, \\ c_1 = & \dfrac{1}{2} - \dfrac{\sqrt{3}}{6}, \qquad c_2 = \dfrac{1}{2} + \dfrac{\sqrt{3}}{6}, \\ t_1 = & t + c_1\Delta t, \qquad t_2 = t + c_2\Delta t. \end{cases} \tag{21}$$

2.2.2 $\Gamma_4^{[4]}$

We have tried another fourth-order method, $\Gamma_4^{[4]}$.[59] It is designed for Hamiltonian functions that can be decomposed into two parts:

$$H(y(t),t) = T + V(y(t),t)\,, \tag{22}$$

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

$$\begin{aligned}\Gamma_4^{[4]} &= \exp\{-i\Delta t\tilde{V}_4\} \\ &\quad \exp\{-i\frac{\Delta t}{2}(T+\tilde{V}_3)\} \\ &\quad \exp\{-i\frac{\Delta t}{2}(T+\tilde{V}_2)\} \\ &\quad \exp\{-i\Delta t\tilde{V}_1\},\end{aligned}$$

where:

$$\begin{cases} \tilde{V}_1 = & a_{11}V_1 + a_{12}V_2 + a_{13}V_3, \\ \tilde{V}_2 = & a_{21}V_1 + a_{22}V_2 + a_{23}V_3, \\ \tilde{V}_3 = & a_{23}V_1 + a_{22}V_2 + a_{21}V_3, \\ \tilde{V}_4 = & a_{13}V_1 + a_{12}V_2 + a_{11}V_3, \end{cases} \tag{23}$$

and

$$V_1 = V[t + c_1\Delta t], \qquad V_2 = V[t + c_2\Delta t], \qquad V_3 = V[t + c_3\Delta t], \tag{24}$$

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:

$$\begin{cases} a_{11} = \dfrac{10+\sqrt{15}}{180}, & a_{12} = -\dfrac{1}{9}, & a_{13} = \dfrac{10-\sqrt{15}}{180}, \\ a_{21} = \dfrac{10+8\sqrt{15}}{180}, & a_{22} = \dfrac{2}{3}, & a_{23} = \dfrac{10+8\sqrt{15}}{180}, \\ c_1 = \dfrac{1}{2} - \dfrac{\sqrt{15}}{10}, & c_2 = \dfrac{1}{2}, & c_3 = \dfrac{1}{2} + \dfrac{\sqrt{15}}{10}, \end{cases} \tag{25}$$

The derivation of this method, relies on the definition of three "generators" α_i:

$$\alpha_1 = -i\Delta t(T + V_2) \tag{26a}$$

$$\alpha_2 = -i\Delta t\frac{\sqrt{15}}{3}(V_3 - V_1) \tag{26b}$$

$$\alpha_3 = -i\Delta t\frac{10}{3}(V_3 - 2V_2 + V_1), \tag{26c}$$

For the method to have fourth order accuracy, the second and third generator must commute, $[\alpha_2, \alpha_3] = 0$. In our case, the division of the Hamiltonian must be done for both the quantum and the classical subsystems:

$$\begin{aligned} H(y(t),t) &= \begin{pmatrix} H_C(q(t),\varphi(t),t) & 0 \\ 0 & H_{\mathrm{KS}}(q(t),\varphi(t),t) \end{pmatrix} \\ &= \begin{pmatrix} T_C + V_C(q(t),\varphi(t),t) & 0 \\ 0 & T_Q + V_Q(q(t),\varphi(t),t) \end{pmatrix} . \end{aligned} \tag{27}$$

Likewise, one may define the corresponding classical and quantum generators α_{Ci} and α_{Qi}, respectively, that 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. For the classical Hamiltonian, Eq. (9), a choice must be made. We have found that simply doing $T_C = 0$ and $V_C(q(t),\varphi(t),t) = H_C(q(t),\varphi(t),t)$ is appropriate, and $[\alpha_{C2}, \alpha_{C3}] = 0$.

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:

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

The potential terms $\tilde{V}_i$ are linear combinations of V_1, V_2, and V_3, which are defined in Eq. (24). The cuadrature points c_i are the same as in $\Gamma_4^{[4]}$, given in Eq. (25).

2.2.4 $\Gamma_4^{[6]}$

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

$$\begin{aligned}\Gamma_4^{[6]} &= \exp\{-i\Delta t(\tilde{V}_4 + \Delta t^2\tilde{V})\} \\ &\quad \exp\{-i\Delta t/2(T + \tilde{V}_3)\} \\ &\quad \exp\{-i\Delta t/2(T + \tilde{V}_2)\} \\ &\quad \exp\{-i\Delta t(\tilde{V}_1 + \Delta t^2\tilde{V})\}\,. \end{aligned} \tag{28}$$

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:

$$\tilde{V} = i\frac{y}{\Delta t^3}\left[\alpha_2, [\alpha_1, \alpha_2]\right]\,, \tag{29}$$

where $y = 1/43200$, and α_i are the generators defined in Eqs. (26).

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 advantangeous to include some commuators if they are easy to compute. This is of course problem – and implementation – dependent. As in all cases, the classical and quantum part can be treated separately:

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

  $$\tilde{V}_Q = i\frac{y}{\Delta t^3}\left[\alpha_{Q2},[\alpha_{Q1},\alpha_{Q2}]\right] \ , \tag{30}$$

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

  $$\tilde{V}_Q = -\frac{1}{25900}||\nabla V_{Q3} - \nabla V_{Q1}||^2, \tag{31}$$

  For the efficiency of the method, it is important that this term can be computed with ease, or otherwise be very small, such that it can be neglected.

- For the nuclear case, the equation reads:

  $$\begin{aligned} \begin{pmatrix} q(t+\Delta t) \\ v(t+\Delta t) \end{pmatrix} &= \exp\{-i\Delta t(\tilde{H}_{C4} + \Delta t^2 \tilde{H}_C)\} \\ & \exp\{-i\Delta t/2\tilde{H}_{C3}\} \\ & \exp\{-i\Delta t/2\tilde{H}_{C2}\} \\ & \exp\{-i\Delta t(\tilde{H}_{C1} + \Delta t^2 \tilde{H}_C)\} \begin{pmatrix} q(t) \\ v(t) \end{pmatrix} \end{aligned} \tag{32}$$

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

  $$H_{Cj} = H_C[t_j] = i\begin{pmatrix} 0 & 1 \\ \lambda_j & 0 \end{pmatrix} \ , \tag{33}$$

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

$$\tilde{H}_C = i \frac{y}{\Delta t^3} \left[\alpha_{C2}, \left[\alpha_{C1}, \alpha_{C2}\right]\right] = \frac{i}{51840} \begin{pmatrix} 0 & 0 \\ (\lambda_3 - \lambda_1)^2 & 0 \end{pmatrix} . \tag{34}$$

3 Results

We have analyzed the performance of these CFM methods for hybrid systems, by simulating a Hydrogen molecule in the presence of a laser field. For this purpose we have used the octopus code,[60,61] 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 $R = 10$ a.u., containing a regular rectangular grid with a spacing of $h = 0.4$ a.u. The total simuation time was set to $T = 20\pi$ a.u. The molecule was subject to the effect of a laser pulse $e(t)$ with the shape

$$e(t) = A \sin(\omega t), \tag{35}$$

where the amplitude is set $A = 0.1$ a.u. and the frequency is $\omega = 10$.

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:

$$E_{\mathrm{wf}} = \sqrt{\sum_m ||\varphi_m(T) - \varphi_m^{\mathrm{exact}}(T)||^2}, \tag{36}$$

where $\varphi_m^{\mathrm{exact}}$ 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, both as the wall-time in seconds for a full run of the simulation, and as the number of Hamiltonian applications for each method. The cost was plotted as a function of the wave function error previously defined.

Figures 1 and 2 summarize the results of the simulations for the EMR and the four CFM methods described above. Fig. 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 the accuracy order of the propagator. We can see that the CFM integrators are significantly more precise than the EMR, with a difference of at least 1.5 orders of magnitude for the values of Δt presented. In this figure, the CFM methods of a given order are indistinguishable, as they produce results with almost equal accuracy.

In Figure 2 we present with solid lines the cost (in seconds) of the propagation, and with dashed lines the cost in number of evaluations of the Hamiltonian, both as a function of the error in the wave function. The axes are again in logarithmic scale. While the cost is completely dependent of the system and the hardware used for the simulation, the number of evaluations of the Hamiltonian is an intrinsic property of each method, making it a suitable 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 depend 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.

As we can see, our results are no exception for that rule: both the cost in terms of wall time and in terms of Hamiltonian evaluations show the same behavior: The order 6 CFM methods are more efficient than their order 4 counter parts when the required error falls below $\sim 10^{-7}$; in particular $\Gamma_4^{[6]}$ is superior to all the other methods in this range of error. For errors $> 10^{-7}$, in contrast, the order 4 propagators show the best performance, $\Gamma_2^{[4]}$ being slightly superior to $\Gamma_4^{[4]}$. And, in all cases, the EMR is completely outclassed by the CFM propagators.

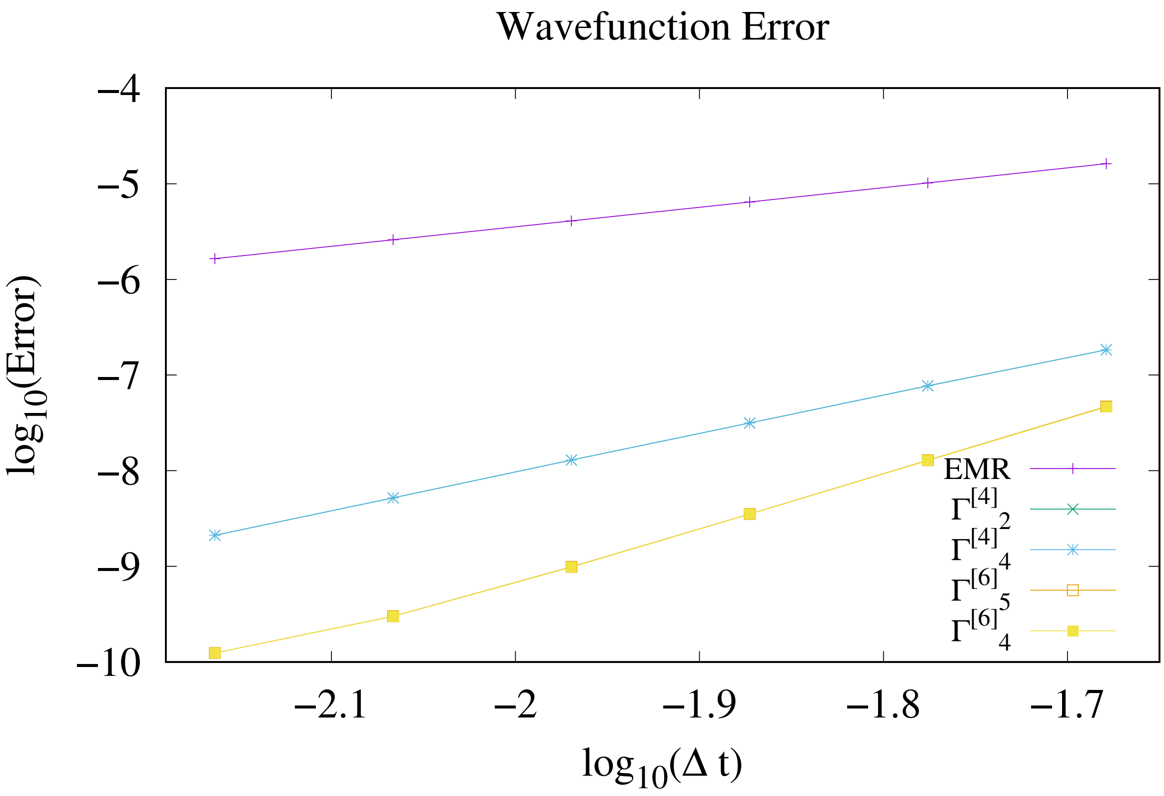

Figure 1: Error in the propagation, measured as the difference of the propagated KS orbital with respect to the quasi-exact one (computed with a tiny time step), as a function of the time step. Both the error and the time step are shown in logarithmic scale.

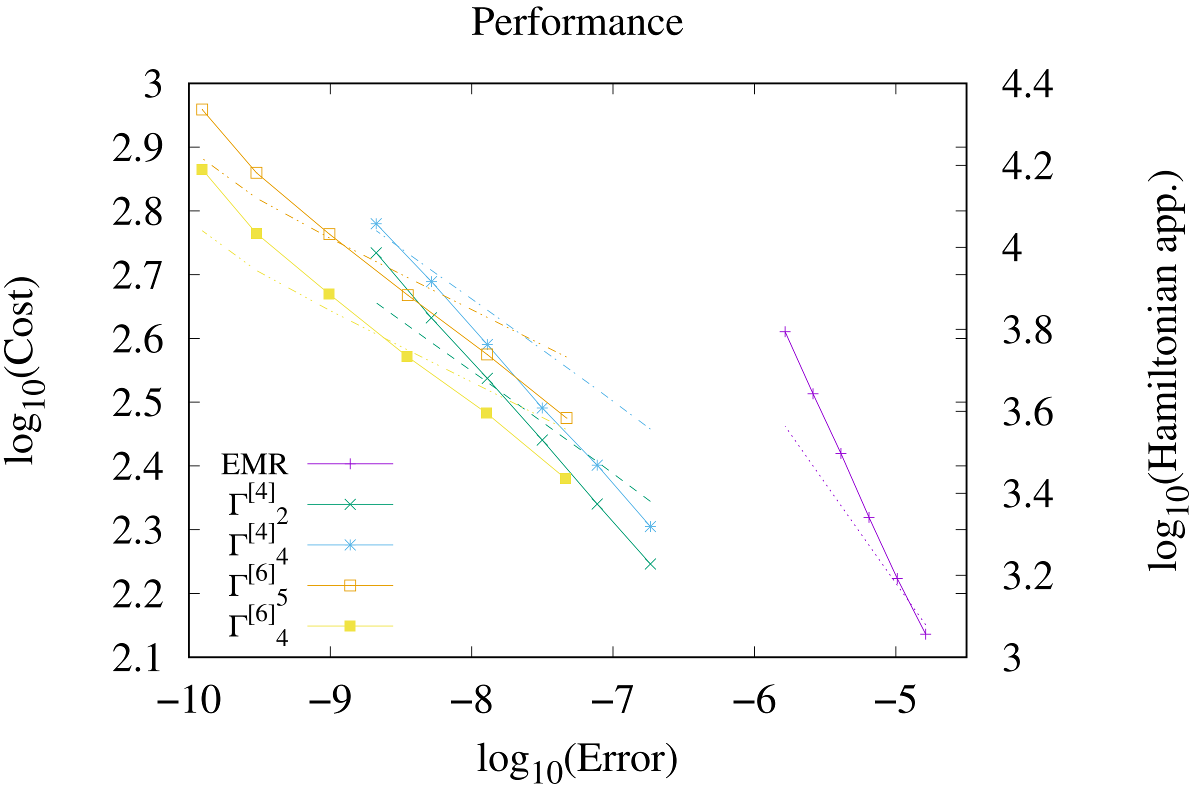

Figure 2: Cost in seconds (scale in left axis) and total number of Hamiltonian applications (scale in the right axis) as a function of the error. The order 6 CFM methods overtake the order 4 ones as the best propagators for errors smaller than 10^{-8}, all of them performing better than the EMR.

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. 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 method.

Instead of using different and independent propagators for the classical and quantum parts, we have rewritten the full dynamics as a non-linear 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, that was developed for *linear* systems. The formulas for propagating the system a given time step requires of 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.

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. 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.

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