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Performance of fourth and sixth-order commutator-free Magnus expansion integrators for Ehrenfest dynamics

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Summary

Hybrid quantum-classical systems combine both classical and quantum degrees of freedom. Typically, in Chemistry, Molecular Physics or Materials Science, the classical degrees of freedom describe atomic nuclei (or cations with frozen core electrons), whereas the quantum particles are the electrons. Although many possible hybrid dynamical models exist, the basic one is the so-called Ehrenfest dynamics, that results from the straightforward partial classical limit applied to the full quantum Schrödinger equation. Few numerical methods have been developed specifically for the integration of this type of systems. Here we present a preliminary study of the performance of a family of recently developed propagators: the (quasi) commutator-free Magnus expansions. These methods, however, were initially designed for non-autonomous linear equations. We employ them for the non-linear Ehrenfest system, by approximating the state value at each time step in the propagation, using an extrapolation from previous time steps.

KEYWORDS:
quantum-classical systems, Magnus expansion, Molecular Dynamics, propagators

1 | INTRODUCTION

If the classical approximation may be taken for a number of particles of a quantum system, but not for others, the problem calls for a hybrid quantum-classical model representation, that may significantly reduce the computational cost with respect to the full quantum treatment. In the extreme case, the quantum degrees of freedom can actually be integrated out completely, leading to a purely classical system, formed by particles that interact through forces that contain in an approximate way the influence of the quantum particles. This is the realm of classical Molecular Dynamics[1] (MD). The problem then reduces to the integration of Newton's equations, and is no longer hybrid but merely classical.

Broadly speaking, this drastic reduction of the complexity of the problem can only be done when the quantum particles (hereafter, the electrons) are constantly in the ground state of the Hamiltonian corresponding to each instantaneous configuration of the classical particles (hereafter, the nuclei). This amounts to assuming the so-called *adiabatic* approximation. Outside its domain of validity, a *non-adiabatic* form of MD must be used,

in which the dynamical system does contain both the electrons and nuclei, that must be evolved simultaneously. A number of hybrid quantum-classical non-adiabatic MD models have been proposed over the years, but perhaps the most fundamental of them all is given by the so-called Ehrenfest equations – oftentimes simply called the mixed quantum-classical dynamics.

This fundamental role played by Ehrenfest dynamics (ED) may be understood in two ways. First of all, it is the result of the straightforward application of the classical limit, for a subset of the particles, to the full Schrödinger equation [2]. Second, it is the Hamiltonian system that results of the simple composition of two Hamiltonian systems that represent both a classical and a quantum part: as it is well known, Schrödinger dynamics may be written in terms of a Poisson bracket, and is therefore a Hamiltonian system [3]. ED is thus symplectic, and it is desirable that the numerical integrator used to solve the ED equations preserves this geometrical structure. Moreover, the norm of the quantum wave function must also be preserved in time.

In principle, the different nature of the particles suggests the use of two different numerical propagators, as their equations of motion – although coupled – are rather different. This is the approach that has often been taken, also favored by the fact that the speed of the particles are normally different by as much as three orders of magnitude – the fact that makes it possible to separate the two sets of particles and take the classical approximation for the heavy and slow ones. Normally, a Verlet or velocity-Verlet algorithm is used for the nuclei, coupled in some way to some propagator designed for linear equations to handle the Schrödinger equation. However, it is desirable to develop schemes that explicitly consider the two subsystems on the same footing, in particular with the purpose of ensuring that the above-mentioned properties (symplecticity, norm conservation) are preserved. Unfortunately, few methods have been specifically designed with this purpose. [4,5,6,7,8,9,10,11]

Recently, some of the present authors [12] have demonstrated the good performance of the commutator free (CF) Magnus expansion [13,14] based propagators for the time-dependent Kohn-Sham equations, which are the set of equations that stem of time-dependent density-functional theory (TDDFT) [15,16]. This theory is one of the many alternatives that exist to tackle the many-electron problem, substituting the Schrödinger equation by more manageable (yet approximate) equations. This substitution reduces the dimension of the problem, making it computationally feasible, but also makes it non-linear (a transformation that is common to most of the other electronic structure methods). The CF Magnus propagators were originally designed for linear equations, yet we proved that they can be used for the non-linear TDDFT equations by performing a simple extrapolation predictor step.

In this proceedings article, we extend this idea to hybrid quantum-classical systems, and present preliminary results on the performance of two order 4 and two order 6 CF Magnus expansion propagators applied to ED – for the case in which the quantum problem is handled directly by Schrödinger's equation. The goal is to use the same propagator for both electrons and nuclei, and apply the CF expansions formula to the full ED, that is also a non-linear problem. In a forthcoming publication [17] we will present the application of these methods to the ED+TDDFT combination, a more detailed analysis of the performance of the schemes, and a deeper theoretical analysis.

Section 2 presents ED, and the specific model for which the numerical results will be later presented (a one-dimensional H_2 molecule with non-interacting electrons). In section 3 we present the Magnus expansion and some CF Magnus integrators that are benchmarked in this work, and

how they are adapted for ED. In section 4 we present the numerical results of the methods, and conclusions are summarized in section 5. Atomic units ($e^2 = \hbar = m_e = a_0 = 1$) will be used hereafter.

2 | EHRENFEST DYNAMICS

Usually, ED is derived as the result of taking a partial classical limit on the Schrödinger for a set of particles [2]. However, one may arrive to ED in an alternative manner that emphasizes its symplectic structure. First of all, let us recall that any quantum system may be rewritten in Hamiltonian form by considering, as canonical coordinates (q_i, p_i) the real and imaginary parts of the coefficients c_i of the system state in any orthonormal basis:

$$c_i = \frac{1}{\sqrt{2}}(q_i + ip_i)\,, \tag{1}$$

where $c_i = \langle\varphi_i|\Psi\rangle$, being Ψ the state of the system, and $\{\varphi_i\}$ an orthonormal basis. Each state Ψ is in this way associated to a set of coordinates, $\Psi = \Psi(q, p)$. One may then prove that Schrödinger's equation for Ψ is equivalent to a Hamiltonian system, i.e.:

$$\dot{q}_i = \frac{\partial H}{\partial p_i}\,, \tag{2}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}\,, \tag{3}$$

where the Hamiltonian function is given by the expectation value of the quantum Hamiltonian operator, $\hat{H}$: $H(q, p) = \langle\Psi(q, p)|\hat{H}|\Psi(q, p)\rangle$. One may then define the standard Poisson bracket, and the dynamics would be given by:

$$\dot{q}_i = \{q_i, H\}_Q\,, \tag{4}$$

$$\dot{p}_i = \{p_i, H\}_Q\,. \tag{5}$$

The "Q" subscript is used to underline the fact that, despite its classical appearance, this is in fact a reformulation of Schrödinger equation.

Suppose now that we also have a classical system characterized by its canonical variables (Q_i, P_i), and its associated classical Poisson bracket $\{\cdot,\cdot\}_C$. We may form a hybrid quantum-classical system by considering all combined degrees of freedom. The dynamical functions ("observables", including the Hamiltonian) of this hybrid functions are then functions defined on the full (q, p, Q, P)-space. However, in order to preserve the quantum character of the quantum subsystem, the only valid functions are those that can be written as expectation values of (Q, P)-dependent self-adjoint linear operators in the Hilbert space. For example, a Hamiltonian can be defined as:

$$H(q, p, Q, P) = \langle\Psi(q, p)|\hat{H}(Q, P)|\Psi(q, p)\rangle\,. \tag{6}$$

A pure classical observable in this context would be given by a real function $A(q, p)$ times the identity operator in the Hilbert space.

The simple sum of both brackets defines then a valid hybrid bracket for the combined system (i.e. it verifies the necessary properties that define a Poisson bracket, i.e. anticommutativity, bilinearity, Leibniz's rule, and the Jacobi identity):

$$\{\cdot,\cdot\}_{\mathrm{H}} = \{\cdot,\cdot\}_{\mathrm{C}} + \{\cdot,\cdot\}_{\mathrm{Q}}\,. \tag{7}$$

Given the Hamiltonian function, the dynamics is then determined by:

$$\dot{\mathsf{q}}_{\mathsf{i}} \;=\; \{\mathsf{q}_{\mathsf{i}},\mathsf{H}\}_{\mathrm{H}}\,, \tag{8}$$

$$\dot{\mathsf{p}}_{\mathsf{i}} \;=\; \{\mathsf{p}_{\mathsf{i}},\mathsf{H}\}_{\mathrm{H}}\,, \tag{9}$$

$$\dot{\mathsf{Q}}_{\mathsf{i}} \;=\; \{\mathsf{Q}_{\mathsf{i}},\mathsf{H}\}_{\mathrm{H}}\,, \tag{10}$$

$$\dot{\mathsf{P}}_{\mathsf{i}} \;=\; \{\mathsf{P}_{\mathsf{i}},\mathsf{H}\}_{\mathrm{H}}\,. \tag{11}$$

These equations are indeed a reformulation of Ehrenfest's equations, found more frequently as:

$$\dot{\mathsf{Q}}_{\mathsf{i}} \;=\; \langle\Psi|\frac{\partial\hat{\mathsf{H}}(\mathsf{Q},\mathsf{P})}{\partial\mathsf{P}_{\mathsf{i}}}|\Psi\rangle\,, \tag{12}$$

$$\dot{\mathsf{P}}_{\mathsf{i}} \;=\; -\langle\Psi|\frac{\partial\hat{\mathsf{H}}(\mathsf{Q},\mathsf{P})}{\partial\mathsf{Q}_{\mathsf{i}}}|\Psi\rangle\,, \tag{13}$$

$$|\dot{\Psi}\rangle \;=\; -\mathsf{i}|\hat{\mathsf{H}}(\mathsf{Q},\mathsf{P})|\Psi\rangle\,. \tag{14}$$

This construction of ED emphasizes its symplectic structure, and the convenience of using a numerical integrator that preserves it. Likewise, it is also easy to see that the norm of the quantum wave function is also a constant of motion.

Despite the simplification entailed by the use of classical variables and equations for part of the system, the many-electron wave function Ψ may be an enormous object, and the solution of the quantum part of the equations grows badly with the number of electrons. For this reason, one normally uses reformulations of these equations, such as time-dependent Hartree-Fock, post-Hartree Fock equations, or TDDFT. In this work, however, we restrict the study to a model system whose unrestricted Schrödinger equation can be handled directly. It corresponds with a one-dimensional model for a Hydrogen molecule, irradiated by an electric field in the dipole approximation:

$$\hat{H}(Q,P,t) = \left(\sum_{\alpha=1,2}\frac{1}{2M}P_\alpha^2 + \frac{1}{|Q_1-Q_2|} - \varepsilon(t)\sum_{\alpha=1,2}Q_\alpha\right)\hat{I} + \sum_{i=1,2}\frac{1}{2}\hat{p}_i^2 - \sum_{i=1,2}\sum_{\alpha=1,2}\frac{1}{\sqrt{1+(Q_\alpha-\hat{x}_i)^2}} + \varepsilon(t)\sum_{i=1,2}\hat{x}_i \tag{15}$$

The quantum operators $\hat{\mathsf{x}}_{\mathsf{i}}, \hat{\mathsf{p}}_{\mathsf{i}}$ are the position and momentum operators, respectively (not to mistake with the q, p variables defined above). M is the Hydrogen nucleus mass (the electron mass is one in atomic units). Notice that we have ignored the electron-electron interaction, so that we may describe the electron wave function with a single-electron doubly occupied orbital $\Psi(\mathrm{x})$. Also notice that the electron nucleus interaction is not a pure Coulomb function, but a "soft-Coulomb" one, a common artifact used in 1D models to avoid the Coulomb singularity [18]. The resulting

equations of motion are then given by:

$$\dot{Q}_\alpha = \frac{1}{M} P_\alpha \,, \tag{16a}$$

$$\dot{P}_\alpha = -\frac{\partial}{\partial Q_\alpha} \frac{1}{|Q_1 - Q_2|} + \varepsilon(t) - 2 \int d^3x |\Psi(x)|^2 \frac{\partial}{\partial Q_\alpha} \frac{1}{\sqrt{1 + (Q_\alpha - x)^2}} \,, \tag{16b}$$

$$i\frac{\partial}{\partial t}\Psi(x) = \left[-\frac{1}{2}\frac{\partial^2}{\partial x^2} - \sum_{\alpha=1,2} \frac{1}{\sqrt{1 + (Q_\alpha - x)^2}} + \varepsilon(t)x \right] \Psi(x) \,. \tag{16c}$$

We have implemented this model and the algorithms described below in the octopus code; for details regarding the numerics see the articles that describe this code [19,20].

3 | COMMUTATOR-FREE MAGNUS EXPANSION METHODS FOR EHRENFEST DYNAMCIS

Let us first recall the general definition of the Magnus expansion propagators. The solution to a linear system,

$$\dot{y}(t) = -iA(t)y(t) \,, \tag{17a}$$

$$y(0) = y_0 \,. \tag{17b}$$

can be written as:

$$y(t + \Delta t) = \exp(\Omega(t + \Delta t, t))y(t) \,, \tag{18}$$

where $\Omega(t + \Delta t, t)$ can be written, at least in a neighbourhood of t, as

$$\Omega(t + \Delta t, t) = \sum_{k=1}^{\infty} \Omega_k(t + \Delta t, t) \,. \tag{19}$$

The existence of this expansion was proved by Magnus [13] in 1954. He also provided a recursive formula for the Ω_k operators, that are given in terms of nested commutators of growing order:

$$\Omega_1(t + \Delta t, t) = \int_t^{t+\Delta t} d\tau_1 (-iA(\tau_1)) \,, \tag{20a}$$

$$\Omega_2(t + \Delta t, t) = \frac{1}{2} \int_t^{t+\Delta t} d\tau_1 \int_t^{\tau_1} d\tau_2 \left[-iA(\tau_1), -iA(\tau_2) \right] \,. \tag{20b}$$

$$\text{etc.} \tag{20c}$$

A working algorithm can be obtained by (1) truncating the infinite series at some cutoff term, and (2) approximating the time integrals with some quadrature formula. The order of accuracy with respect to Δt can be systematically improved by increasing the truncated series size (and consistently increasing the quadrature formula order). The trade-off for this accuracy improvement is the computational complexity, specially due to the need to obtain the action of the nested commutators. This need is absent in the simplest member of this family, the second order method that

results of truncating the series at $k = 1$, and using just one quadrature point: the exponential midpoint rule (EMR):

$$y(t + \Delta t) = \exp(-i\Delta t A(t + \Delta t/2))y(t)\,. \tag{21}$$

The commutator-free approximations to the Magnus expansions[21] were invented to alleviate this difficulty. They are given by expressions in the form:

$$y(t + \Delta t) = \Gamma_M^{[S]}(A)y(t), \tag{22a}$$

$$\Gamma_M^{[S]}(A) = \prod_{k=1}^{M} \exp\left[-i\Delta t \sum_{\mu}^{K} \alpha_{k\mu} A(\tau_\mu)\right], \tag{22b}$$

where M is the number of exponentials of the method, S is the accuracy order of the resulting method and $\tau_\mu = t + c_\mu \Delta t$ are some time points within the interval $[t, t + \Delta t]$. In some cases, as we shall see below, the operators appearing on the right-hand-side are not always the full matrix $A(\tau_\mu)$, but parts of it. Notice that for a given k, if $\sum_\mu^N \alpha_{k\mu} = 0$ then the constant parts of A in this exponential disappear. The simplest member of this family is also the EMR, that in this notation would be denoted as $\Gamma_1^{[2]}$.

In this work, in addition to this EMR, we have focused on the following higher order formulas:

- Order 4:

  One fourth order method that requires of only two exponentials was reported in Refs. 21 and 22. It is given by:

$$\Gamma_2^{[4]}(A) = \exp\{-i\Delta t(a_{11}A[t_1] + a_{12}A[t_2])\}\exp\{-i\Delta t(a_{12}A[t_1] + a_{11}A[t_2])\}\,, \tag{23}$$

  The constants a_{ij} and t_i are:

$$\begin{cases} a_{11} = & \dfrac{3 - 2\sqrt{3}}{12}, & a_{12} = \dfrac{3 + 2\sqrt{3}}{12}, \\ c_1 = & \dfrac{1}{2} - \dfrac{\sqrt{3}}{6}, & c_2 = \dfrac{1}{2} + \dfrac{\sqrt{3}}{6}, \\ t_1 = & t + c_1\Delta t, & t_2 = t + c_2\Delta t. \end{cases} \tag{24}$$

  Another fourth-order method, that is computationally more expensive yet allegedly more precise, was suggested by Bader *et al.*[23] It makes use of four exponentials (and therefore we will denote it $\Gamma_4^{[4]}$). This apparently makes it in principle more expensive to compute, yet this extra cost is not so significant whenever the dynamical matrix A can be split in two pieces:

$$A(t) = T + V(t)\,. \tag{25}$$

  The first term, the "kinetic" operator T, is time-independent, whereas the second "potential" term $V(t)$ is such that the exponential is easy to calculate (for example, because it is diagonal). This is indeed the case in the type of problems that we are addressing. The method is then defined as:

$$\Gamma_4^{[4]}(A) = \exp\{-i\Delta t\tilde{V}_4\}\exp\{-i\frac{\Delta t}{2}(T + \tilde{V}_3)\}\exp\{-i\frac{\Delta t}{2}(T + \tilde{V}_2)\}\exp\{-i\Delta t\tilde{V}_1\}, \tag{26}$$

where we make use of the following linear combinations

$$\begin{cases} \tilde{V}_1 = & a_{11}V_1 + a_{12}V_2 + a_{13}V_3, \\ \tilde{V}_2 = & a_{21}V_1 + a_{22}V_2 + a_{23}V_3, \\ \tilde{V}_3 = & a_{23}V_1 + a_{22}V_2 + a_{21}V_3, \\ \tilde{V}_4 = & a_{13}V_1 + a_{12}V_2 + a_{11}V_3, \end{cases} \tag{27}$$

of the potential term at different instants in time:

$$V_1 = V(t + c_1\Delta t), \qquad V_2 = V(t + c_2\Delta t), \qquad V_3 = V(t + c_3\Delta t), \tag{28}$$

If the two exponentials that only involve potential terms are easy to calculate, then in practice the cost of this method is comparable to that of $\Gamma_2^{[4]}$. The value of all the constants that appear in the previous equations may be consulted in Ref. [23].

- Order 6:

We have tested an order six method that requires five exponentials, $\Gamma_5^{[6]}$. However, it can profit from the same division of the matrix into a kinetic and a potential term described for $\Gamma_4^{[4]}$: two exponentials are then in principle cheaper, as they only involve potential terms:

$$\Gamma_5^{[6]}(A) = \exp\{-i\Delta t\tilde{V}_5\}\exp\{-i\Delta t(b_1 T + \tilde{V}_4)\}\exp\{-i\Delta t(b_2 T + \tilde{V}_3)\}\exp\{-i\Delta t(b_1 T + \tilde{V}_2)\}\exp\{-i\Delta t\tilde{V}_1\}, \tag{29}$$

The potential operators $\tilde{V}_i$ are linear combinations of V_1, V_2, and V_3, which are defined in Eq. (28). The cuadrature points c_i are the same as in $\Gamma_4^{[4]}$.

Finally, we have also implemented a four-exponential sixth-order method, $\Gamma_4^{[6]}$:

$$\Gamma_4^{[6]}(A) = \exp\{-i\Delta t(\tilde{V}_4 + \Delta t^2\tilde{V})\}\exp\{-i(\Delta t/2)(T + \tilde{V}_3)\}\exp\{-i(\Delta t/2)(T + \tilde{V}_2)\}\exp\{-i\Delta t(\tilde{V}_1 + \Delta t^2\tilde{V})\}\,. \tag{30}$$

The potential terms $\tilde{V}_i$ are once again linear combinations of V_1, V_2 and V_3. There is a new term, $\tilde{V}$, given by:

$$\tilde{V} = i\frac{1}{43200\Delta t^3}\,[\alpha_2, [\alpha_1, \alpha_2]]\,, \tag{31}$$

where α_1 and α_2 are the first two of the three "generators" of the Lie algebra that is used to derive and analyze the properties of these methods[14]:

$$\alpha_1 = -i\Delta t(T + V_2) \tag{32a}$$

$$\alpha_2 = -i\Delta t\frac{\sqrt{15}}{3}(V_3 - V_1) \tag{32b}$$

$$\alpha_3 = -i\Delta t\frac{10}{3}(V_3 - 2V_2 + V_1), \tag{32c}$$

In purity, given Eq. [31], this method is no longer a CF scheme. However, it can be considered a *quasi*-CF method, if these commutators in particular are not difficult to compute – as it will be shown below for the case that we are considering.

The previous method definitions assume a linear (possibly non-autonomous) system such as the one introduced in Eqs. 17. Yet our ED [Eqs. 16] is not linear. Let us start by rewriting it in a more compact way. We define the full state vector as:

$$y = \begin{bmatrix} Q \\ V \\ \Psi \end{bmatrix} \tag{33}$$

where Q and V are all the positions and velocities of the nuclei. Ehrenfest's equations may then be written as:

$$\begin{pmatrix} \dot{Q}(t) \\ \dot{V}(t) \\ \dot{\psi}(t) \end{pmatrix} = -i \begin{pmatrix} H_C(Q(t), \Psi(t), t) & 0 \\ 0 & H_Q(Q(t), t) \end{pmatrix} \begin{pmatrix} Q(t) \\ V(t) \\ \Psi(t) \end{pmatrix}. \tag{34}$$

We have introduced a "classical" Hamiltonian matrix H_C:

$$H_C(Q(t), \Psi(t), t) = i \begin{pmatrix} 0 & 1 \\ \frac{F(Q(t), \Psi(t), t)}{m Q(t)} & 0 \end{pmatrix}. \tag{35}$$

where the force $F(Q(t), \Psi(t), t)$ is the right hand side of Eq. 16b. The "quantum" Hamiltonian $H_Q(Q(t), t)$ is then given by the right hand side of Eq. 16c. Note that in order to arrive to the form of a non-linear Schrödinger equation, 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.

In compact form, defining a "total" Hamiltonian $H_T(y(t), t)$ given by the full matrix in Eq. 34, it becomes clear that we do have an equation in the form of a non-linear Schrödinger-like equation:

$$\dot{y}(t) = -i H_T(y(t), t) y(t). \tag{36}$$

Yet the CF algorithms described above are only defined for linear systems. Looking at the general formula [Eq. 22], one needs the Hamiltonian at K times τ_μ, within the propagating interval $[t, t + \Delta t]$. In a non-linear problem, this Hamiltonian is unknown. It may however be approximated by making use, at each time step, of the state of the system at previous time steps and performing an extrapolation; in the following we will call $H_T[\tau_\mu]$ to the Hamiltonian computed from these extrapolated states.

Once we have a way to approximate the state (and therefore, the Hamiltonian terms) at the intermediate steps, we may apply the general formula. In our hybrid case, the block-diagonal structure of the matrix allows to perform the propagations independently:

$$\begin{pmatrix} Q(t + \Delta t) \\ V(t + \Delta t) \end{pmatrix} = \Gamma_M^{[S]}(H_C) \begin{pmatrix} Q(t) \\ V(t) \end{pmatrix}, \tag{37}$$

$$\Psi(t+\Delta t) = \Gamma_M^{[S]}(H_Q)\Psi(t)\,. \tag{38}$$

Before moving on to describing some numerical results, a few remarks:

1. In order to preserve the order of accuracy of the algorithm with respect to Δt, the extrapolation must be performed with a formula of equal or larger order to the one of the method (4 or 6, in our case). This implies a cost in terms of memory, since the states of previous time steps must be stored. The computational cost, however, is not significant (although this may be problem dependent).

2. We must specify how to split both H_Q and H_C into the T and V(t) terms. For the quantum case, the division is obvious, as we do have a real kinetic term and a potential term (whose exponential is fast to compute, as it is a diagonal operator in real space). For the classical part of the Hamiltonian, H_C, various choices are possible; in the examples shown below, we have simply set $T = 0$.

4 | RESULTS

We have assessed the accuracy, and benchmarked the performance, of the methods described above, by performing calculations with the model shown in Section 2. We show here results for one sample calculation, that summarizes the key results. In this case, the Hydrogen molecule was subjet to a sinusoidal electric field:

$$\varepsilon(t) = A\sin(\omega t)\,. \tag{39}$$

We set the amplitude to A $= 0.1$ a.u., and the frequency to $\omega = 10$ a.u. The simulation was followed for 100 periods, i.e. up to $T = 100\frac{2\pi}{\omega}$ a.u. At the end, the propagated wave function was compared to a quasi-exact result, obtained by propagating the system using an explicit sixth order Runge-Kutta method with a very small time step. The error was defined as:

$$E = \left(\int \mathrm{d}x\, |\Psi(x,T) - \Psi_{\mathrm{exact}}(x,T)|^2\right)^{1/2}. \tag{40}$$

We could add the error in the nuclear coordinates, but we found that this suffices to get a qualitative idea of the methods performance.

In Fig. 1 we display, for one sample calculation, the error obtained with the five methods, as a function of the time step Δt. Both scales are logarithmic, and in principle the slope of the curves in the limit $\Delta t \to 0$ should coincide with the accuracy order of each method. The key findings are:

1. The higher order methods greatly improve the accuracy with respect to the lowest order ones. Obviously, this difference grows as Δt approaches zero, or in other words, if greater accuracy is required.

2. The EMR has a very clear order two slope. In contrast, both the order four and order six methods have a more irregular behaviour, and their expected order is only observed approximately.

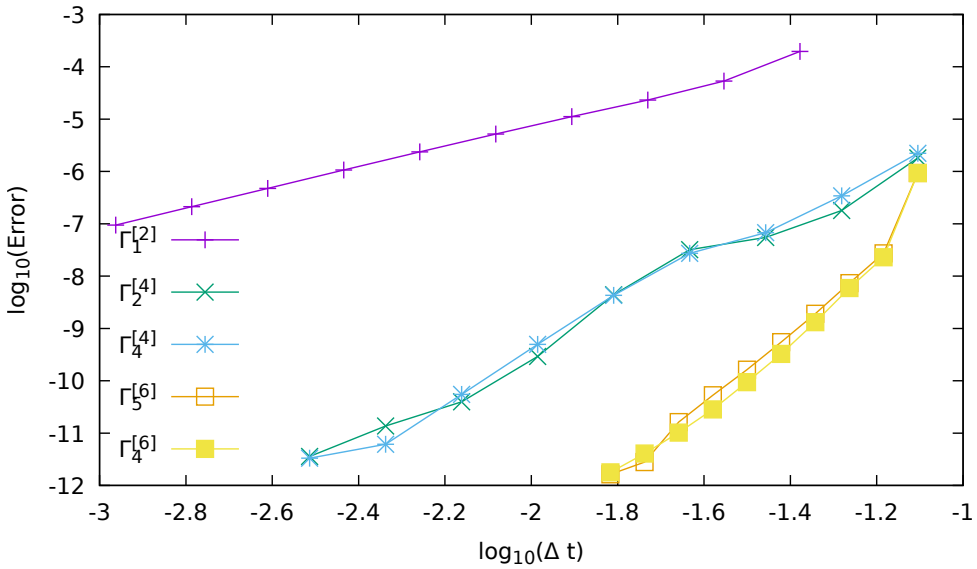

FIGURE 1 Propagation error (formula given in Eq. 40), as a function of the time step Δt (both in logarithmic scale), for the five methods discussed in the text.

3. These CF methods applied to non-linear systems have an extra source of error in comparison with the same method applied to linear systems: the extrapolation. We have tried both a normal Lagrange polynomial form, and also the Newton-Gregory extrapolation formula, with similar results. In any case, these add an extra error term whose order with respect to Δt is given by the number of previous states stored and used in the formula. For the cases that we have studied (this may be problem dependent), if the extrapolation is done at the same order than the underlying method, the extrapolation error dominates. We therefore perform the extrapolations of larger order (8 when using the 6th order expansions, 6 when using the 4th order expansions).

Finally, in Fig. 2 we plot the wall time cost of the calculations, with respect to the accuracy achieved in each of the runs. This plot permits to decide which of the methods is the most efficient for a given required level of accuracy. It becomes clear that the higher the accuracy, the more convenient that it is to use higher-order, more sophisticated methods. Comparing the two order six methods, it is also clear that $\Gamma_4^{[6]}$ is faster, even if one needs the extra cost of computing the potential derivatives. The comparison of the two order 4 methods is however less conclusive. The EMR could become advantageous only when very little accuracy is required. Although these findings are problem dependent, we have observed very similar behaviour in many of our test runs.

5 | CONCLUSIONS

The accuracy and performance of some members of the CF Magnus expansion family of propagators was benchmarked when applied to the non-linear Ehrenfest equations problem that describe hybrid quantum-classical systems. The procedure to do so consists in rewriting Ehrenfest equations in the form of a non-linear Schrödinger equation, and then using an extrapolation technique to predict the Hamiltonian at future times,

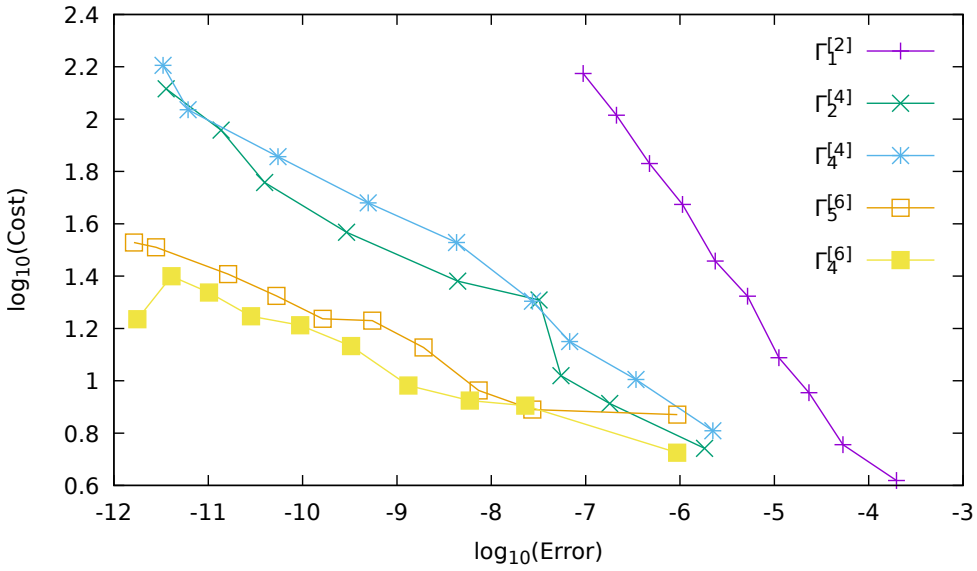

FIGURE 2 Propagation cost (wall clock time in seconds), as a function of the propagation error (both in logarithmic scale), for the five methods discussed in the text.

as required by the algorithms. In this way, the two subsystems (classical and quantum) are treated on the same footing, and therefore the properties of the methods are not compromised by the coupling of the equations. The use of Magnus expansions ensures the preservation of geometrical properties – such as the symplectic structure and the wave function norm.

It was shown how these methods are accurate and fast alternatives. The advantage of using them, in contrast to simpler schemes (such as the EMR, or a simple second-order Verlet algorithm for the nuclei coupled to any general purpose scheme for the electrons), should become specially apparent if high precisions are required. The use of the extrapolation does not spoil the good behaviour already found for linear systems.

The quantum subsystem was handled directly by Schrödinger's equation. Work is in progress on the extension of the problem to the case in which this equation is substituted by the non-linear Kohn-Sham equations of time-dependent density-functional theory (TDDFT), which will make possible the use of these techniques for larger and more realistic systems.

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