Analysis of the Toolkit method for the time-dependant Schrödinger equation

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ANALYSIS OF THE TOOLKIT METHOD FOR THE TIME-DEPENDANT SCHRÖDINGER EQUATION

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Abstract. The goal of this paper is to provide an analysis of the "toolkit" method used in the numerical approximation of the time-dependent Schrödinger equation. The "toolkit" method is based on precomputation of elementary propagators and was seen to be very efficient in the optimal control framework. Our analysis shows that this method provides better results than the second order Strang operator splitting. In addition, we present two improvements of the method in the limit of low and large intensity control fields.

1. Introduction

The control of the evolution of molecular systems at the quantum level has been a long standing goal ever since the beginning of the laser technology. After an initial slowed down of the investigations in this area due to unsuccessful experiments, the realization that the problem can be recast and attacked with the tools of (optimal) control theory [10] greatly contributed to the first positive experimental results [1, 11, 12, 19, 20]. Ever since, the desire to understand theoretically how the laser acts to control the molecule lead the investigators to resort to numerical simulations which require repeated resolution of the Time Dependent Schrödinger Equation of the type (1); additional motivation comes from related contexts (online identification algorithms, learning algorithms, quantum computing [7], etc.).

The numerical method used to solve the time dependent Schrödinger equation must provide accurate results without prohibitive computational cost. The conservation of the L^2 norm of the wave function $\psi(x,t)$ is also generally required for stability and as a mean of qualitative validation of the numerical solution.

In this context, the second order Strang operator splitting is often considered [4, 8, 18]. However, this method suffers from two drawbacks. First, the numerical error is proportional to the norm of the control which implies poor accuracy when dealing with large laser fields $\varepsilon(t)$ and make necessary the use of small time steps. Secondly, it requires at each time step three matrix products. This difficulty is enhanced in some particular settings e.g., in optimal control, where the matrices involved in the control term must be assembled online.

Recently introduced, the "toolkit method" [21, 22] solves this last problem by precomputing a set of elementary matrices, used in the numerical resolution. Each matrix is associated to (one or several) field values and enables to solve the evolution over one time step. This algorithm has been used in various frameworks and shows excellent results. It has also been coupled successfully with optimal control and identification issues [3]. The dependence on the L^∞-norm of the control, which is a restriction of the Strang method, is also improved by the "toolkit method" as it will be shown in our analysis.

The goal of the paper is to provide a (first) numerical analysis of the "toolkit method". Our mathematical tools are related to that in [4] (but for a different

setting; see also [9, 16] for connected results); the treatment here is different because of the quantization appearing in the values of the control $\varepsilon(t)$ which impacts both the mathematical analysis and the numerical efficiency of the method. The analysis enables us to propose two possible improvements.

The paper is organized as follows: after having introduced the model and some notations in Section 2, the toolkit method is presented and analyzed in Section 3. An improvement of this method in the limit of small control fields is introduced in Section 4. A second improvement, in the limit of large control fields is given in Section 5. Finally, Section 6 gathers some numerical results.

2. Model and notations

In this section, we present the Schrödinger Equation that will be considered in the paper and some useful notations.

We consider the time dependent Schrödinger equation (TDSE)

$$\left\{ \begin{array}{ll} i\partial_t \psi(x,t) = (H_0(x) - \mu(x)\varepsilon(t))\psi(x,t), & \mathbb{R}^3 \times (0,T) \\ \psi(x,0) = \psi_0(x), & \mathbb{R}^3. \end{array} \right. \tag{1}$$

This equation governs the evolution of a quantum system, described by its wave function ψ, that interacts with a laser pulse of amplitude ε, the control variable. The factor μ is the dipole moment operator of the system. The Hamiltonian of the system is $H_0 = -\Delta_x + V$ where Δ_x is the Laplacian operator over the space variables and $V = V(x)$ the electrostatic potential in which the system evolves. We refer to [13] for more details about models involved in quantum control. Note that to obtain Eq. (1), one has considered the laser effect as a perturbative term, so that the control term $\varepsilon(t)\mu(x)$ is obtained through a first order approximation with respect to $\varepsilon(t)$. While often considered, this approximation fails at describing some models involving non linear laser-dipole interaction, see e.g. [15]. Consequently, the norm of the field cannot be always considered as a small parameter, and numerical solvers have to tolerate large controls, as the one described here after.

Throughout this paper, $T > 0$ is the time of control of a quantum system. The space $L^p(0,T;X)$, with $p \in [1,+\infty)$ denotes the usual Lebesgue space taking its values in a Banach space X. The notation $W^{1,1}(0,T)$ corresponds to the space of time dependent functions belonging to $L^1(0,T;\mathbb{R})$ such that their first time derivative also belongs to $L^1(0,T)$. We denote by L^2 the space $L^2(\mathbb{R}^3,\mathbb{C})$ and by $W^{2,\infty}$ and H^2 the Sobolev spaces $W^{2,\infty}(\mathbb{R}^3,\mathbb{R})$ and $H^2(\mathbb{R}^3,\mathbb{C})$. The space $\mathcal{L}(H^2)$ is the space of linear functionals on H^2. One can refer to [5] (or the introduction of [6]) for more details about the definitions of these functional spaces.

Finally, in order to introduce some numerical solver of (1), let us consider an integer N and $\Delta t > 0$ such that $N\Delta t = T$. We introduce the time discretization $(t_j)_{0\leq j\leq N}$ of $[0,T]$ with $t_j = j\Delta t$ and we also denote by $t_{j+\frac{1}{2}}$ the intermediate time $\frac{t_j+t_{j+1}}{2} = (j+\frac{1}{2})\Delta t$.

Let us first recall some basic results of existence and regularity of the solution of the TDSE. These are corollaries of a general result on time dependent Hamiltonians (see [14], p. 285, Theorem X.70).

Lemma 1. *Let $\mu \in \mathcal{L}(H^2)$, $V \in W^{2,\infty}$, $\varepsilon \in L^2(0,T)$ and $\psi_0 \in H^2$. The Schrödinger equation*

$$\begin{cases} i\partial_t\psi(t) = (H_0 - \mu\varepsilon(t))\,\psi(t) & \mathbb{R}^3 \times (0,T) \\ \psi(0) = \psi_0, & \mathbb{R}^3, \end{cases} \tag{2}$$

has a unique solution $\psi \in L^\infty(0,T;H^2) \cap W^{1,\infty}(0,T;L^2)$ such that

$$\|\psi(t)\|_{L^\infty(0,T;H^2)} + \|\partial_t\psi(t)\|_{L^\infty(0,T;L^2)} \leq C\|\mu\|_{\mathcal{L}(H^2)}\|\varepsilon\|_{W^{1,1}(0,T)}\|\psi_0\|_{H^2}.$$

Moreover, for all $t \in [0,T]$, $\quad \|\psi(t)\|_{L^2} = \|\psi_0\|_{L^2}$.

It is also well known (see [6] for instance) that for any $T > 0$ and $\phi_0 \in H^2$, if we have $\varepsilon(t) = \bar{\varepsilon} \in \mathbb{R}$, independent of time t, the Schrödinger equation

$$\begin{cases} i\partial_t\phi(t) = (H_0 - \mu\bar{\varepsilon})\,\phi(t), & \mathbb{R}^3 \times (0,T) \\ \phi(0) = \phi_0, & \mathbb{R}^3 \end{cases}$$

has a unique solution $\phi(t) = S(t)\phi_0$ such that $\phi \in C([0,T];H^2) \cap C^1([0,T];L^2)$, where $(S(t))_{t\in\mathbb{R}}$ denotes the one-parameter semi-group generated by the operator $H_0 - \mu\bar{\varepsilon}$. Moreover, for all $t \in [0,T]$, $S(t) \in \mathcal{L}(H^2)$ and we have

$$\begin{array}{ll} S(t)\phi_0 \in C(0,T;H^2), & \forall \phi_0 \in H^2; \\ \|S(t)\|_{\mathcal{L}(H^2)} \leq 1 + CT \leq K, & \forall t \in [0,T]; K = K(\|\mu\|_{\mathcal{L}(H^2)}, \varepsilon_{\max}); \\ \|S(t)\phi_0\|_{L^2} = \|\phi_0\|_{L^2}, & \forall \phi_0 \in L^2, \forall t \in \mathbb{R}; \\ S(0) = \mathrm{Id}, & \\ S(t+s) = S(t)S(s), & \forall s,t \in \mathbb{R}. \end{array} \tag{3}$$

Therefore, the solution of Eq. (2) is obtained equivalently as a solution to the integral equation

$$\psi(t) = S(t)\psi_0 + i\int_0^t S(t-s)(\varepsilon(s) - \bar{\varepsilon})\mu\psi(s)\,ds.$$

3. The toolkit method

We now present the toolkit method and describe the corresponding error analysis.

3.1. **Algorithm.**

In this method, we assume that the control field ε satisfies the following hypothesis:

$$\forall t \in [0,T],\ \varepsilon(t) \in [\varepsilon_{\min}, \varepsilon_{\max}]. \tag{$\mathcal{H}$}$$

The values of the control field are discretized according to:

$$\bar{\varepsilon}_\ell = \varepsilon_{\min} + \ell\Delta\varepsilon,\ \ell = 0...m, \tag{4}$$

with $m = \frac{\varepsilon_{\max} - \varepsilon_{\min}}{\Delta\varepsilon}$. Here, the values $\bar{\varepsilon}_\ell$ have been here uniformly chosen in the interval $[\varepsilon_{\min}, \varepsilon_{\max}]$. If some properties of the field are known, e.g. its mean value or its variance, some improvement of the method can be obtained by optimizing the distribution of the values $\bar{\varepsilon}_\ell$. More generally, this topic enters the field of scalar quantization, that will not be considered in this paper. We refer to [17] and the references therein for a review of standard methods in this domain. In order to solve numerically equation (2), the toolkit method proceeds as follows.

Algorithm 1. *(toolkit method)*

(1) *Preprocessing. Precompute the "toolkit", i.e. the set of propagators:*

$$S_\ell(\Delta t) \text{ for } \ell = 0, \cdots, m,$$

where $(S_\ell(t))_{t\in\mathbb{R}}$ *denotes the one-parameter semi-group generated by the operator* $H_0 - \mu\bar{\varepsilon}_\ell$*, the sequence* $(\varepsilon_\ell)_{\ell=0,\cdots,m,}$ *being defined by* (4)*.*

(2) *Given a control field* $\varepsilon \in L^2$ *satisfying* $\mathcal{H}$ *and* $\psi_0^K = \psi_0$*, the sequence* $(\psi_j^K)_{j=0,\ldots,N}$ *that approximates* $(\psi(t_j))_{j=0,\ldots,N}$*, is obtained recursively by iterating the following loop:*

(a) *Find:*

$$\ell_j = \text{argmin}_{\ell=1,\cdots,m}\{|\varepsilon(t_{j+\frac{1}{2}}) - \bar{\varepsilon}_\ell|\},$$

(b) *Set* $\psi_{j+1}^K = S_{\ell_j}(\Delta t)\psi_j^K$*.*

In this "toolkit" approximation, we consider that the changes in the Hamiltonian $H(t) := H_0 - \mu\varepsilon(t)$ can be neglected over a time step Δt. In this way, if $\Delta\varepsilon = 0$ (infinite toolkit), and for a relevant time discretization, the simulation corresponding to piecewise constant control fields is exact. Such a property does not hold with methods that approximate the exponential, e.g. the second order Strang operator splitting. Indeed, these approaches introduce an algebraic error, due to the non-commutation of the operators H_0 and μ that is consequently proportional to $\|\varepsilon\|_{L^\infty(0,T)}$.

Remark 1. *In the original form of the toolkit method* [2, 21, 22]*, the mid-point choice proposed in Step 2a of Algorithm 1 is not considered. Yet, the introduction of this strategy enables us to improve the order of the method (see the analysis hereafter).*

3.2. **Analysis of the method.** Let us now present an error analysis of the toolkit method. More precisely, this section aims at proving the following result:

Theorem 2. *Let* $\varepsilon \in W^{2,\infty}(0,T)$ *and* ψ *the corresponding solution of* (2)*. Let* ψ^K *be the approximation of* ψ *obtained with Algorithm 1. Given* $\Delta t > 0$ *and* $\Delta\varepsilon > 0$*, there exists* $\lambda_1 > 0$*,* $\lambda_2 > 0$*, that do not depend on* $\|\varepsilon\|_{L^\infty(0,T)}$ *such that:*

$$\|\psi(T) - \psi^K(T)\|_{L^2} \leq \lambda_1\Delta\varepsilon + \lambda_2\Delta t^2. \tag{5}$$

Moreover, there exists $\nu_1 > 0$*,* $\nu_2 > 0$ *depending on* $\|\varepsilon\|_{W^{1,1}(0,T)}$ *such that:*

$$\|\psi(T) - \psi^K(T)\|_{H^2} \leq \nu_1\Delta\varepsilon + \nu_2\Delta t^2. \tag{6}$$

Remark 2. *This result shows that the toolkit method enables to work with large control fields, transferring the computational effort due to such cases to the preprocessing step: given* $\Delta\varepsilon$*, the computational cost of this step only depends on the norm* $\|\varepsilon\|_{L^\infty(0,T)}$*, i.e., on Hypothesis* $\mathcal{H}$*.*

Proof. To obtain (5) and (6), we will focus first on the local error, i.e. the approximation obtained on one time step $[t_j, t_{j+1}]$.
The sequence $(\psi_j^K)_{j=0,\ldots,N}$ is a time discretization of the solution of

$$\begin{cases} i\partial_t\psi^K(t) = (H_0 - \mu\bar{\varepsilon}(t))\,\psi^K(t), & \mathbb{R}^3 \times (0,T) \\ \psi^K(0) = \psi_0, & \mathbb{R}^3 \end{cases} \tag{7}$$

where the space variable has been omitted and $\bar{\varepsilon}(t) = \bar{\varepsilon}_{\ell_j}$ is constant over each interval $[t_j, t_{j+1}[= [j\Delta t, (j+1)\Delta t[$, with $j = 0, ..., N-1$. We denote by $(S_j(t))_{j=0,\dots,N-1}$ (instead of S_{ℓ_j}) the one-parameter semi-group generated by the operator $H_0 - \mu\bar{\varepsilon}_{\ell_j}$ and we introduce $\delta(t) = \varepsilon(t) - \bar{\varepsilon}$ where $\bar{\varepsilon}$ (instead of $\bar{\varepsilon}_{\ell_j}$) is the constant value of $\bar{\varepsilon}(t)$ over $[t_j, t_{j+1}]$. Therefore, the solution ψ of (2) is actually the solution of the integral equation, settled for $t \in [t_j, t_{j+1}[$:

$$\psi(t) = S_j(t - t_j)\psi(t_j) + i\int_{t_j}^{t} S_j(t-s)\mu\delta(s)\psi(s)\, ds. \tag{8}$$

For the upcoming calculations, one should notice that we have

$$|\delta(t_{j+\frac{1}{2}})| \leq \frac{\Delta\varepsilon}{2} \tag{9}$$

and that for all $t \in [t_j, t_{j+1}]$,

$$|\delta(t)| \leq \frac{1}{2}\left(\Delta\varepsilon + \|\dot{\varepsilon}\|_{L^\infty(0,T)}\Delta t\right). \tag{10}$$

We consider the following decomposition:

$$\begin{aligned}\psi(T) - \psi^K(T) &= \psi(T) - S_{N-1}(\Delta t)\psi(t_{N-1}) \\ &+ \sum_{j=0}^{N-2} S_{N-1}(\Delta t)\dots S_{j+1}(\Delta t)\big(\psi(t_{j+1}) - S_j(\Delta t)\psi(t_j)\big) \\ &+ S_{N-1}(\Delta t)\dots S_0(\Delta t)\psi_0 - \psi^K(T)\end{aligned}$$

where the last line is equal to 0 since ψ^K satisfies (7) on $[0, T]$.

From now on and in all the following sections, we will consider either that $\|\psi_0\|_{L^2} = 1$ or that $\|\psi_0\|_{H^2} = 1$. From (3), we know that the operators S_j are isometries in L^2. Therefore, the use of a triangular inequality brings

$$\|\psi(T) - \psi^K(T)\|_{L^2} \leq \sum_{j=0}^{N-1} \|\psi(t_{j+1}) - S_j(\Delta t)\psi(t_j)\|_{L^2}. \tag{11}$$

We will thus calculate and estimate in L^2-norm for all j the difference

$$\begin{aligned}\psi(t_{j+1}) - S_j(\Delta t)\psi(t_j) &= i\int_{t_j}^{t_{j+1}} S_j(t_{j+1}-s)\delta(s)\mu\psi(s)\, ds \\ &= i\int_{t_j}^{t_{j+1}} S_j(t_{j+1}-s)\delta(s)\mu\left(\psi(s) - S_j(s-t_j)\psi(t_j)\right) ds \\ &\quad + i\int_{t_j}^{t_{j+1}} S_j(t_{j+1}-s)\delta(s)\mu S_j(s-t_j)\psi(t_j)\, ds. \\ &= i\int_{t_j}^{t_{j+1}} S_j(t_{j+1}-s)\delta(s)\mu\left(\psi(s) - S_j(s-t_j)\psi(t_j)\right) ds \\ &\quad + i\int_{t_j}^{t_{j+1}} \delta(s)\varphi_j(s)\psi(t_j)\, ds \end{aligned} \tag{12}$$

where $\varphi_j(s) := S_j(t_{j+1} - s)\mu S_j(s - t_j) \in \mathcal{L}(L^2)$.

In what follows, we work in parallel on L^2 and H^2-estimates of $\psi(t_{j+1}) - S_j(\Delta t)\psi(t_j)$. We will need basic L^2 and H^2-estimates of $\psi(t) - S_j(t-t_j)\psi(t_j)$ for the study of the first integral term of (12), the second one will be dealt with using a Taylor expansion of $\delta(t)$.

From Lemma 1, (8) and (10), it is easy to obtain coarse estimates of $\psi(t) - S_j(t-t_j)\psi(t_j)$. Indeed, for all t in $[t_j, t_{j+1}]$, one can write

$$\begin{aligned}
\|\psi(t) - S_j(t-t_j)\psi(t_j)\|_{L^2} &= \left\| i\int_{t_j}^{t} S_j(t-s)\mu\delta(s)\psi(s)\ ds \right\|_{L^2} \\
&\leq \int_{t_j}^{t_{j+1}} \|S_j(t-s)\mu\delta(s)\psi(s)\|_{L^2}\ ds \\
&\leq \Delta t\|\mu\|_{\mathcal{L}(L^2)}\frac{1}{2}\left(\Delta\varepsilon + \|\dot{\varepsilon}\|_{L^\infty(0,T)}\Delta t\right)\|\psi_0\|_{L^2} \\
&\leq \frac{1}{2}\|\mu\|_{\mathcal{L}(L^2)}\left(\Delta\varepsilon + \|\dot{\varepsilon}\|_{L^\infty(0,T)}\Delta t\right)\Delta t \qquad (13)
\end{aligned}$$

and the H^2-estimate gives

$$\|\psi(t) - S_j(t-t_j)\psi(t_j)\|_{H^2} \leq K\|\varepsilon\|_{W^{1,1}(0,T)}\|\mu\|_{\mathcal{L}(H^2)}\left(\Delta\varepsilon + \|\dot{\varepsilon}\|_{L^\infty(0,T)}\Delta t\right)\Delta t \qquad (14)$$

where $K = K(\|\mu\|_{\mathcal{L}(H^2)}, \varepsilon_{\max})$ is a generic constant that estimates every $\|S_j\|_{\mathcal{L}(H^2)}$. Therefore, we can obtain more accurate estimates of the first integral term of (12). Thanks to (13), we obtain

$$\begin{aligned}
&\left\| i\int_{t_j}^{t_{j+1}} S_j(t_{j+1}-s)\delta(s)\mu\left(\psi(s) - S_j(s-t_j)\psi(t_j)\right)\ ds \right\|_{L^2} \\
&\leq \frac{1}{2}\|\mu\|_{\mathcal{L}(L^2)}\left(\Delta\varepsilon + \|\dot{\varepsilon}\|_{L^\infty(0,T)}\Delta t\right)\Delta t \sup_{t\in[t_j,t_{j+1}]}\|\psi(s) - S_j(s-t_j)\psi(t_j)\|_{L^2} \\
&\leq \frac{1}{4}\|\mu\|^2_{\mathcal{L}(L^2)}\left(\Delta\varepsilon + \|\dot{\varepsilon}\|_{L^\infty(0,T)}\Delta t\right)^2\Delta t^2 \\
&\leq \frac{1}{2}\|\mu\|^2_{\mathcal{L}(L^2)}\left(\Delta\varepsilon^2 + \|\dot{\varepsilon}\|^2_{L^\infty(0,T)}\Delta t^2\right)\Delta t^2. \qquad (15)
\end{aligned}$$

Working now on the H^2-estimate, we deduce from (14) in the same way that

$$\begin{aligned}
&\left\| i\int_{t_j}^{t_{j+1}} S_j(t_{j+1}-s)\delta(s)\mu\left(\psi(s) - S_j(s-t_j)\psi(t_j)\right)\ ds \right\|_{L^2} \qquad (16) \\
&\qquad\qquad \leq \frac{1}{2}K\|\mu\|_{\mathcal{L}(H^2)}\|\varepsilon\|_{W^{1,1}(0,T)}\left(\Delta\varepsilon^2 + \|\dot{\varepsilon}\|^2_{L^\infty(0,T)}\Delta t^2\right)\Delta t^2.
\end{aligned}$$

In the two cases (L^2 and H^2), estimates are stronger than the ones we look for, and we can focus on the second integral term of (12) we want to deal with.

We first consider

$$\begin{array}{rccl}
\varphi_j : & [t_j, t_{j+1}] & \to & \mathcal{L}(H^2) \\
& s & \mapsto & S_j(t_{j+1}-s)\mu S_j(s-t_j)
\end{array} \qquad (17)$$

and note that for all $\psi \in H^2$, $\|\varphi_j(s)\psi\|_{H^2} = \|S_j(t_{j+1}-s)\mu S_j(s-t_j)\psi\|_{H^2} \leq K\|\psi\|_{H^2}$ so that

$$\forall s \in [t_j, t_{j+1}],\ \|\varphi_j(s)\|_{\mathcal{L}(H^2)} \leq K\|\mu\|_{\mathcal{L}(H^2)}. \tag{18}$$

Let us now consider the derivatives of $\varphi_j(s)$. Since $(S_j(t))_{t\in\mathbb{R}}$ denotes the one-parameter semi-group generated by the operator $H_0 - \mu\bar{\varepsilon}$, the $\mathcal{L}(H^2)$ identity

$$\partial_t S_j(t) = -i\left(H_0 - \mu\bar{\varepsilon}\right) S_j(t)$$

holds and minor calculations give, $\forall s \in [t_j, t_{j+1}]$,

$$\begin{aligned}
\partial_s\varphi_j(s) &= iS_j(t_{j+1}-s)[H_0,\mu]S_j(s-t_j)\\
\partial^2_{ss}\varphi_j(s) &= S_j(t_{j+1}-s)\big[[H_0,\mu], H_0-\mu\bar{\varepsilon}\big]S_j(s-t_j).
\end{aligned}$$

Therefore,

$$\begin{aligned}
\|\partial_s\varphi_j(s)\|_{\mathcal{L}(H^2)} &\leq K\|[H_0,\mu]\|_{\mathcal{L}(H^2)}\\
\|\partial^2_{ss}\varphi_j(s)\|_{\mathcal{L}(H^2)} &\leq K\left\|\big[[H_0,\mu], H_0-\mu\bar{\varepsilon}\big]\right\|_{\mathcal{L}(H^2)}.
\end{aligned} \tag{19}$$

If we consider the L^2-analysis of the method, then $\varphi_j(s) \in \mathcal{L}(L^2)$ and $\forall s \in [t_j, t_{j+1}]$,

$$\begin{aligned}
\|\varphi_j(s)\|_{\mathcal{L}(L^2)} &\leq \|\mu\|_{\mathcal{L}(L^2)}\\
\|\partial_s\varphi_j(s)\|_{\mathcal{L}(L^2)} &\leq \|[H_0,\mu]\|_{\mathcal{L}(L^2)}\\
\|\partial^2_{ss}\varphi_j(s)\|_{\mathcal{L}(L^2)} &\leq \left\|\big[[H_0,\mu], H_0-\mu\bar{\varepsilon}\big]\right\|_{\mathcal{L}(L^2)}.
\end{aligned} \tag{20}$$

Let us now write the third order Taylor expansion of $t \mapsto \delta(t) = \varepsilon(t) - \bar{\varepsilon}$ in a neighborhood of $t_{j+\frac{1}{2}}$:

$$\begin{aligned}
\delta(s) &= \delta(t_{j+\frac12}) + (s-t_{j+\frac12})\dot{\delta}(t_{j+\frac12}) + \frac{1}{2}(s-t_{j+\frac12})^2\ddot{\delta}(\theta(s))\\
&= \delta(t_{j+\frac12}) + (s-t_{j+\frac12})\dot{\varepsilon}(t_{j+\frac12}) + \frac{1}{2}(s-t_{j+\frac12})^2\ddot{\varepsilon}\big(\theta(s)\big),
\end{aligned}$$

with $\theta(s) \in [t_j, t_{j+1}]$. We now focus on estimating the term $i\displaystyle\int_{t_j}^{t_{j+1}} \delta(s)\varphi_j(s)\psi(t_j)\,ds$. By means of (20) and the L^2-norm conservation, we obtain

$$\left\|\int_{t_j}^{t_{j+1}} \delta(t_{j+\frac12})\varphi_j(s)\psi(t_j)ds\right\|_{L^2} \leq \frac{1}{2}\|\mu\|_{\mathcal{L}(L^2)}\Delta\varepsilon\Delta t,$$

$$\begin{aligned}
&\left\|\int_{t_j}^{t_{j+1}} \left(s-t_{j+\frac12}\right)\dot{\varepsilon}\left(t_{j+\frac12}\right)\varphi_j(s)\psi(t_j)ds\right\|_{L^2}\\
&= \left\|\dot{\varepsilon}\left(t_{j+\frac12}\right)\int_0^{\frac12\Delta t} s\,\left(\varphi(t_{j+\frac12}+s) - \varphi(t_{j+\frac12}-s)\right)\psi(t_j)ds\right\|_{L^2}\\
&= \left\|\dot{\varepsilon}\left(t_{j+\frac12}\right)\int_0^{\frac12\Delta t}\int_{t_{j+\frac12}-s}^{t_{j+\frac12}+s} s\partial_u\varphi(u)\psi(t_j)\,duds\right\|_{L^2}\\
&\leq \frac{1}{12}\|[H_0,\mu]\|_{\mathcal{L}(L^2)}\|\dot{\varepsilon}\|_{L^\infty(t_j,t_{j+1})}\Delta t^3
\end{aligned}$$

and

$$\left\| \int_{t_j}^{t_{j+1}} \frac{1}{2} \left(s - t_{j+\frac{1}{2}} \right)^2 \ddot{\varepsilon}(\theta(s)) \varphi_j(s) \psi(t_j) ds \right\|_{L^2} \leq \frac{1}{24} \|\mu\|_{\mathcal{L}(L^2)} \|\ddot{\varepsilon}\|_{L^\infty(t_j, t_{j+1})} \Delta t^3.$$

Combining these results with (15), we estimate (12) as follows:

$$\begin{aligned} \|\psi(t_{j+1}) - S_j(\Delta t)\psi(t_j)\|_{L^2} &\leq \frac{1}{2}\|\mu\|^2_{\mathcal{L}(L^2)} \left(\Delta\varepsilon^2 \Delta t^2 + \|\dot{\varepsilon}\|^2_\infty \Delta t^4 \right) \\ &\quad + \frac{1}{2} \|\mu\|_{\mathcal{L}(L^2)} \Delta\varepsilon \Delta t \\ &\quad + \frac{1}{24} \left(2\|[H_0, \mu]\|_{\mathcal{L}(L^2)} \|\dot{\varepsilon}\|_\infty + \|\mu\|_{\mathcal{L}(L^2)} \|\ddot{\varepsilon}\|_\infty \right) \Delta t^3, \end{aligned}$$

with $\|\cdot\|_{L^\infty(0,T)} = \|\cdot\|_\infty$. By means of (11), the global L^2-estimate is then:

$$\begin{aligned} \|\psi(T) - \psi^K(T)\|_{L^2} &\leq \sum_{j=0}^{N-1} \|\psi(t_{j+1}) - S_j(\Delta t)\psi(t_j)\|_{L^2} \\ &\leq \frac{T}{2}\|\mu\|^2_{\mathcal{L}(L^2)} \left(\Delta\varepsilon^2 \Delta t + \|\dot{\varepsilon}\|^2_\infty \Delta t^3 \right) + \frac{T}{2} \|\mu\|_{\mathcal{L}(L^2)} \Delta\varepsilon \\ &\quad + \frac{T}{24} \left(2\|[H_0, \mu]\|_{\mathcal{L}(L^2)} \|\dot{\varepsilon}\|_\infty + \|\mu\|_{\mathcal{L}(L^2)} \|\ddot{\varepsilon}\|_\infty \right) \Delta t^2, \end{aligned}$$

and (5) can be deduced with the following constants λ_1 and λ_2 independent of $\|\varepsilon\|_{L^\infty(0,T)}$:

$$\begin{aligned} \lambda_1 &= \frac{T}{2}\|\mu\|_{\mathcal{L}(L^2)} \left(1 + \Delta\varepsilon \Delta t \|\mu\|_{\mathcal{L}(L^2)} \right), \\ \lambda_2 &= \frac{T}{2} \|\mu\|^2_{\mathcal{L}(L^2)} \|\dot{\varepsilon}\|^2_\infty \Delta t + \frac{T}{12} \|[H_0, \mu]\|_{\mathcal{L}(L^2)} \|\dot{\varepsilon}\|_\infty + \frac{T}{24} \|\mu\|_{\mathcal{L}(L^2)} \|\ddot{\varepsilon}\|_\infty. \end{aligned}$$

Let us now prove the H^2 estimate. By means of (16), (18) and (19) and keeping in mind that K is a generic constant depending on $\|\mu\|_{\mathcal{L}(H^2)}$ and $\varepsilon_{\max}$, we can repeat the previous analysis to find the local estimate:

$$\begin{aligned} \|\psi(t_{j+1}) - S_j(\Delta t)\psi(t_j)\|_{H^2} &\leq K\|\mu\|_{\mathcal{L}(H^2)} \|\varepsilon\|_{W^{1,1}(0,T)} \left(\Delta\varepsilon^2 \Delta t^2 + \|\dot{\varepsilon}\|^2_{L^\infty(0,T)} \Delta t^4 \right) \\ &\quad + K\Delta\varepsilon\Delta t + K\Big(\|[H_0, \mu]\|_{\mathcal{L}(H^2)} \|\dot{\varepsilon}\|_{L^\infty} + \|\ddot{\varepsilon}\|_{L^\infty} \Big) \Delta t^3. \end{aligned}$$

Since one can prove that we can actually write a more precise estimate of $S_j(\Delta t)$ and replace K by $1 + C\Delta t$ (see properties (3)), we get:

$$\|S_j(\Delta t)\|_{\mathcal{L}(H^2)} \leq 1 + C\Delta t.$$

and since we have the following intermediate result, where $M > 0$ depends on $\|\mu\|_{\mathcal{L}(H^2)}$, $\varepsilon_{\max}$ and T but is independent of N:

$$\sum_{j=0}^{N-1} (1 + C\Delta t)^{N-j} \Delta t \leq M.$$

The global estimate is obtained as follows:

$$\begin{aligned}
\|\psi(T)-\psi^K(T)\|_{H^2} &\leq \sum_{j=0}^{N-1} K^{N-j-1}\|\psi(t_{j+1})-S_j(\Delta t)\psi(t_j)\|_{H^2} \\
&\leq \sum_{j=0}^{N-1}(1+C\Delta t)^{N-j}\|\varepsilon\|_{W^{1,1}(0,T)}\left(\Delta\varepsilon^2\Delta t^2+\|\dot\varepsilon\|_\infty^2\Delta t^4\right) \\
&\quad + \sum_{j=0}^{N-1}(1+C\Delta t)^{N-j}\left(\Delta\varepsilon\Delta t+\left(\|[H_0,\mu]\|_{\mathcal{L}(H^2)}\|\dot\varepsilon\|_\infty+\|\ddot\varepsilon\|_\infty\right)\Delta t^3\right) \\
&\leq M\|\varepsilon\|_{W^{1,1}(0,T)}\left(\Delta\varepsilon^2\Delta t+\|\dot\varepsilon\|_\infty^2\Delta t^3\right)+M\Delta\varepsilon \\
&\quad + M\left(\|[H_0,\mu]\|_{\mathcal{L}(H^2)}\|\dot\varepsilon\|_\infty+\|\ddot\varepsilon\|_\infty\right)\Delta t^2.
\end{aligned}$$

We finally get ν_1 and ν_2 and conclude the proof of Theorem 2:

$$\begin{aligned}
\nu_1 &= M(1+\|\varepsilon\|_{W^{1,1}(0,T)}T\Delta\varepsilon\Delta t) \\
\nu_2 &= M\left(\|\varepsilon\|_{W^{1,1}(0,T)}\|\dot\varepsilon\|_\infty^2\Delta t+\|[H_0,\mu]\|_{\mathcal{L}(H^2)}\|\dot\varepsilon\|_\infty+\|\ddot\varepsilon\|_\infty\right).
\end{aligned}$$

□

Remark 3. *The estimate* (5) *is consistent with the fact that Algorithm 1 used with a relevant time discretization is exact for the piecewise constant control fields.*

4. Improvement in the limit of low intensities

We now describe a way to improve the time order of the previous algorithm. Since some constants in the following analysis depend in this case of the L^∞-norm of the field and the method requires that the toolkit size scales $\Delta t^3(\varepsilon_{\max}-\varepsilon_{\min})$, it applies in the case of (L^∞-) small control fields.

4.1. Algorithm.

The algorithm we propose mixes the toolkit and the splitting approaches, in the sense that it applies sequentially various operators to correct the third order local error that appears in the proof of Theorem 2.

Algorithm 2. *(Improved toolkit method for low intensities)*

(1) *Preprocessing. Precompute the "toolkit", i.e. the set of propagators:*

$$S_\ell(\Delta t) \text{ for } \ell=0,\cdots,m,$$

where $(S_\ell(t))_{t\in\mathbb{R}}$ denotes the one-parameter group generated by the operator $H_0-\mu\bar\varepsilon_\ell$, the sequence $(\varepsilon_\ell)_{\ell=0,\cdots,m}$, being defined by (4)*. Include in this set the two special elements:*

$$\Omega=e^{\frac{1}{12}[H_0,\mu]\Delta t^3},\Theta=e^{\frac{i}{24}\mu\Delta t^3}$$

and the initial exponents α_0 and β_0 such that (ε being extended as an even function on [-T,0]):

$$\begin{aligned}
\alpha_0 &:= \frac{\varepsilon(\Delta t)-\varepsilon(0)}{\Delta t}=\dot\varepsilon(t_{\frac12})+\mathcal{O}(\Delta t^2), \\
\beta_0 &:= \frac{\varepsilon(t_1)-2\varepsilon(t_{\frac12})+\varepsilon(0)}{\Delta t^2}=\ddot\varepsilon(t_{\frac12})+\mathcal{O}(\Delta t^2).
\end{aligned}$$

(2) *Given a control field* $\varepsilon \in L^\infty$ *satisfying* $\mathcal{H}$ *and* $\psi_0^{IK} = \Omega^{\alpha_0}\Theta^{\beta_0}\psi_0$*, the sequence* $(\psi_j^{IK})_{j=0,\dots,N}$ *that approximates* $(\psi(t_j))_{j=0,\dots,N}$*, is obtained recursively by iterating the following loop:*

(a) *Find:*

$$\ell_j = \text{argmin}_{\ell=1,\cdots,m}\{|\varepsilon(t_{j+1/2}) - \bar{\varepsilon}_\ell|\},$$

(b) *Compute* α_j *and* β_j *such that:*

$$\alpha_j := \frac{\varepsilon(t_{j+1}) - \varepsilon(t_j)}{\Delta t} = \dot{\varepsilon}(t_{j+\frac{1}{2}}) + \mathcal{O}(\Delta t^2), \tag{21}$$

$$\beta_j := \frac{\varepsilon(t_{j+1}) - 2\varepsilon(t_{j+\frac{1}{2}}) + \varepsilon(t_j)}{\Delta t^2} = \ddot{\varepsilon}(t_{j+\frac{1}{2}}) + \mathcal{O}(\Delta t^2). \tag{22}$$

(c) *Set* $\psi_{j+1}^{IK} = S_{\ell_j}(\Delta t)\Omega^{\alpha_j}\Theta^{\beta_j}\psi_j^{IK}$.

In many cases, e.g. in the experimental frameworks, only the values of the field can be handled. The use of exact values for the time derivatives has then to be avoided when possible. This motivates the introduction of approximations (21) and (22) of $\dot{\varepsilon}(t_j)$ and $\ddot{\varepsilon}(t_j)$ in the latest definitions. The analysis presented hereafter shows that this does not deteriorate the order of the method.

In this method, one must perform two online matrices exponentiations. By working in a basis where one of these two matrices is diagonal, the cost of Step *2c* can be reduced to one exponentiation, making the cost of this method equivalent the second order Strang operator splitting.

4.2. **Analysis of the method.** We can now repeat the analysis that has been done in the proof of Theorem 2 to obtain the following estimate.

Theorem 3. *Let* $\varepsilon \in W^{2,\infty}(0,T)$*,* ψ *be the corresponding solution of* (2) *and* ψ^{IK} *the approximation of* ψ *obtained with Algorithm 2. Given* $\Delta t > 0$ *and* $\Delta\varepsilon > 0$*, there exists* $\lambda_1' > 0$*,* $\lambda_2' > 0$*, with* λ_1' *independent of* $\|\varepsilon\|_{L^\infty(0,T)}$ *such that:*

$$\|\psi(T) - \psi^{IK}(T)\|_{L^2} \leq \lambda_1'\Delta\varepsilon + \lambda_2'\Delta t^3.$$

Proof. In the framework of this new algorithm, we note that on every time interval $]t_j, t_{j+1}[$, the approximation ψ^{IK} is the solution of the evolution equation:

$$\begin{cases} i\partial_t\psi^{IK}(t) &= (H_0 - \mu\bar{\varepsilon})\,\psi^{IK}(t), \quad \mathbb{R}^3 \times (t_j, t_{j+1}) \\ \psi^{IK}(t_j^+) &= \Omega^{\alpha_j}\Theta^{\beta_j}\psi^{IK}(t_j^-) \qquad \mathbb{R}^3 \end{cases} \tag{23}$$

where we set $\psi(0^-) = \psi_0$. We will keep the notations (S_j, $\delta(t)$, φ,...) of the proof of Theorem 2, and we first focus on the local error analysis. We consider the following

decomposition:

$$\begin{aligned}\psi(T)-\psi^{IK}(T) &= \psi(T)-S_{N-1}(\Delta t)\Omega^{\alpha_{N-1}}\Theta^{\beta_{N-1}}\psi(t_{N-1})\\ &+\sum_{j=0}^{N-2} S_{N-1}(\Delta t)\Omega^{\alpha_{N-1}}\Theta^{\beta_{N-1}}\dots S_{j+1}(\Delta t)\Omega^{\alpha_{j+1}}\Theta^{\beta_{j+1}}\\ &\qquad\times\left(\psi(t_{j+1})-S_j(\Delta t)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\right)\\ &+ S_{N-1}(\Delta t)\Omega^{\alpha_{N-1}}\Theta^{\beta_{N-1}}\dots S_0(\Delta t)\Omega^{\alpha_0}\Theta^{\beta_0}\psi_0-\psi^{IK}(T)\end{aligned}$$

where the last line is equal to 0 since ψ^{IK} satisfies (23) on $[0,T]$.
The operators S_j are isometries in L^2, we will consider that $\|\psi_0\|_{L^2}=1$ and we also have, for all j

$$\Omega^{\alpha_j}\Theta^{\beta_j}=e^{\frac{\alpha_j}{12}[H_0,\mu]\Delta t^3}e^{\frac{i\beta_j}{24}\mu\Delta t^3}=\mathrm{Id}+\left(\frac{\alpha_j}{12}[H_0,\mu]+\frac{i\beta_j}{24}\mu\right)\Delta t^3+\mathrm{Id}\,\mathcal{O}(\Delta t^6) \tag{24}$$

and thus

$$\left\|\Omega^{\alpha_j}\Theta^{\beta_j}\right\|_{\mathcal{L}(L^2)}\leq 1+\mathcal{O}(\Delta t^3). \tag{25}$$

Therefore, the use of a triangular inequality brings

$$\|\psi(T)-\psi^{IK}(T)\|_{L^2}\leq(1+\mathcal{O}(\Delta t^2))\sum_{j=0}^{N-1}\left\|\psi(t_{j+1})-S_j(\Delta t)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\right\|_{L^2} \tag{26}$$

and we will calculate and estimate in L^2-norm for all j the difference

$$\begin{aligned}&\psi(t_{j+1})-S_j(\Delta t)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\\ =\;& S_j(\Delta t)\psi(t_j)+i\int_{t_j}^{t_{j+1}}S_j(t_{j+1}-s)\delta(s)\mu\psi(s)\,ds-S_j(\Delta t)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\\ =\;& S_j(\Delta t)\left(\mathrm{Id}-\Omega^{\alpha_j}\Theta^{\beta_j}\right)\psi(t_j)+i\int_{t_j}^{t_{j+1}}S_j(t_{j+1}-s)\delta(s)\mu\psi(s)\,ds.\end{aligned}$$

We define $Y(s)=\psi(s)-S_j(s-t_j)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)$ for all $s\in[t_j,t_{j+1}]$ and obtain

$$\begin{aligned}Y(t_{j+1}) &= S_j(\Delta t)\left(\mathrm{Id}-\Omega^{\alpha_j}\Theta^{\beta_j}\right)\psi(t_j)\\ &+i\int_{t_j}^{t_{j+1}}S_j(t_{j+1}-s)\delta(s)\mu Y(s)\,ds+i\int_{t_j}^{t_{j+1}}\delta(s)\varphi_j(s)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\,ds\end{aligned} \tag{27}$$

where $\varphi_j(s):=S_j(t_{j+1}-s)\mu S_j(s-t_j)$ and its derivatives have been estimated in L^2 in (20). As we did in Theorem 2, we start with an estimate of the first integral term of (27). For all $t\in]t_j,t_{j+1}]$, we can write:

$$\begin{aligned}Y(t) &= \psi(t)-S_j(t-t_j)\psi(t_j)+S_j(t-t_j)\psi(t_j)-S_j(t-t_j)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\\ &= \int_{t_j}^{t}S_j(t-s)\delta(s)\mu\psi(s)\;ds+S_j(t-t_j)\left(\mathrm{Id}-\Omega^{\alpha_j}\Theta^{\beta_j}\right)\psi(t_j).\end{aligned}$$

Moreover, for all $t\in]t_j,t_{j+1}]$, we have

$$\|Y(t)\|_{L^2}\leq\left\|\int_{t_j}^{t}S_j(t-s)\delta(s)\mu\psi(s)\;ds\right\|_{L^2}+\left\|S_j(t-t_j)\left(\mathrm{Id}-\Omega^{\alpha_j}\Theta^{\beta_j}\right)\psi(t_j)\right\|_{L^2}$$

The operators S_j are isometries in L^2 and $\forall t \in [0,T], \|\psi(t)\|_{L^2} = \|\psi_0\|_{L^2}$. Therefore, we deduce from (24) that

$$\left\|S_j(t-t_j)\left(\mathrm{Id} - \Omega^{\alpha_j}\Theta^{\beta_j}\right)\psi(t_j)\right\|_{L^2} \leq \left(\frac{\alpha_j}{12}\left\|[H_0,\mu]\right\|_{\mathcal{L}(L^2)} + \frac{i\beta_j}{24}\left\|\mu\right\|_{\mathcal{L}(L^2)}\right)\Delta t^3 + \mathcal{O}(\Delta t^6).$$

Since it is clear that we also have

$$\left\|\int_{t_j}^{t} S_j(t-s)\delta(s)\mu\psi(s)\ ds\right\|_{L^2} \leq \frac{1}{2}\|\mu\|_{\mathcal{L}(L^2)}\left(\Delta\varepsilon + \|\dot{\varepsilon}\|_{L^\infty(0,T)}\Delta t\right)\Delta t,$$

one can finally deduce that:

$$\begin{aligned} & \left\|i\int_{t_j}^{t_{j+1}} S_j(t_{j+1}-s)\delta(s)\mu Y(s)\ ds\right\|_{L^2} \\ \leq\ & \frac{1}{2}\|\mu\|_{\mathcal{L}(L^2)}\left(\Delta\varepsilon + \|\dot{\varepsilon}\|_{L^\infty(0,T)}\Delta t\right)\Delta t \sup_{t\in[t_j,t_{j+1}]}\|Y(t)\|_{L^2} \\ \leq\ & \frac{1}{4}\|\mu\|^2_{\mathcal{L}(L^2)}\left(\Delta\varepsilon + \|\dot{\varepsilon}\|_{L^\infty(0,T)}\Delta t\right)^2\Delta t^2 + \mathcal{O}(\Delta\varepsilon\Delta t^4) + \mathcal{O}(\Delta t^5). \end{aligned} \tag{28}$$

We focus now on the first and third terms of (27). Using (24), we get

$$S_j(\Delta t)\left(\mathrm{Id} - \Omega^{\alpha_j}\Theta^{\beta_j}\right)\psi(t_j) = -S_j(\Delta t)\left(\frac{\alpha_j}{12}[H_0,\mu] + \frac{i\beta_j}{24}\mu\right)\psi(t_j)\Delta t^3 + \psi(t_j)\mathcal{O}(\Delta t^6).$$

Let us then consider the second integral term of (27). On the one hand, we consider the fourth order expansion of $\delta = \varepsilon - \bar{\varepsilon}$ in a neighborhood of $t_{j+\frac{1}{2}}$:

$$\begin{aligned} \delta(s) &= \delta(t_{j+\frac{1}{2}}) + (s-t_{j+\frac{1}{2}})\dot{\delta}(t_{j+\frac{1}{2}}) + \frac{1}{2}(s-t_{j+\frac{1}{2}})^2\ddot{\delta}(t_{j+\frac{1}{2}}) + \frac{1}{6}(s-t_{j+\frac{1}{2}})^3\delta^{(3)}(\theta(s)) \\ &= \delta(t_{j+\frac{1}{2}}) + (s-t_{j+\frac{1}{2}})\dot{\varepsilon}(t_{j+\frac{1}{2}}) + \frac{1}{2}(s-t_{j+\frac{1}{2}})^2\ddot{\varepsilon}(t_{j+\frac{1}{2}}) + \frac{1}{6}(s-t_{j+\frac{1}{2}})^3\varepsilon^{(3)}\big(\theta(s)\big) \end{aligned}$$

where $\theta(s) \in [t_j, t_{j+1}]$. On the other hand, we calculate and/or estimate the four corresponding terms in

$$i\int_{t_j}^{t_{j+1}} \delta(s)\varphi_j(s)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\,ds.$$

From (9) and (20), the term of order 0 gives:

$$\left\|i\int_{t_j}^{t_{j+1}} \delta(t_{j+\frac{1}{2}})\varphi_j(s)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)ds\right\|_{L^2} \leq \frac{1}{2}\|\mu\|^2_{\mathcal{L}(L^2)}\Delta\varepsilon\Delta t.$$

For the term of order 1, we can write

$$\begin{aligned}
& i\int_{t_j}^{t_{j+1}} (s-t_{j+\frac{1}{2}})\dot{\varepsilon}(t_{j+\frac{1}{2}})\varphi_j(s)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\ ds \\
= \ & i\,\dot{\varepsilon}\left(t_{j+\frac{1}{2}}\right)\int_0^{\frac{1}{2}\Delta t} s\big(\varphi_j(t_{j+\frac{1}{2}}+s)-\varphi_j(t_{j+\frac{1}{2}}-s)\big)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\ ds \\
= \ & i\,\dot{\varepsilon}\left(t_{j+\frac{1}{2}}\right)\int_0^{\frac{1}{2}\Delta t}\int_{t_{j+\frac{1}{2}}-s}^{t_{j+\frac{1}{2}}+s} s\partial_u\varphi_j(u)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\ duds \\
= \ & i\,\dot{\varepsilon}(t_{j+\frac{1}{2}})\int_0^{\frac{1}{2}\Delta t}\int_{t_{j+\frac{1}{2}}-s}^{t_{j+\frac{1}{2}}+s} s\big(\partial_u\varphi_j(t_j)+(u-t_j)\tau(u)\big)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\ duds \\
= \ & \frac{\dot{\varepsilon}(t_{j+\frac{1}{2}})}{12}S_j\left(\Delta t\right)[H_0,\mu]\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\Delta t^3 \\
& + i\,\dot{\varepsilon}(t_{j+\frac{1}{2}})\int_0^{\frac{1}{2}\Delta t}\int_{t_{j+\frac{1}{2}}-s}^{t_{j+\frac{1}{2}}+s} s(u-t_j)\tau(u-t_j)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\ duds \\
= \ & \frac{\alpha_j}{12}S_j\left(\Delta t\right)[H_0,\mu]\psi(t_j)\Delta t^3 + S_j\left(\Delta t\right)[H_0,\mu]\psi(t_j)\mathcal{O}(\Delta t^6) \\
& + i\,\dot{\varepsilon}(t_{j+\frac{1}{2}})\int_0^{\frac{1}{2}\Delta t}\int_{t_{j+\frac{1}{2}}-s}^{t_{j+\frac{1}{2}}+s} s(u-t_j)\tau(u-t_j)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\ duds
\end{aligned}$$

where we used (21), (24) and (20) and the function $\tau : s \in [0,\Delta t] \mapsto \tau(s) \in \mathcal{L}(L^2)$ is defined as the function that appears in the following expansion of $\partial_u\varphi_j$ around t_j, for any $\psi \in L^2$

$$\begin{aligned}
\partial_u\varphi_j(u)\psi &= \partial_u\varphi_j(t_j)\psi + (u-t_j)\tau(u-t_j)\psi \\
&= iS_j(\Delta t)[H_0,\mu]\psi + (u-t_j)\tau(u-t_j)\psi.
\end{aligned}$$

Using the estimate (coming from (20))

$$\|\tau(s)\|_{\mathcal{L}(L^2)} \leq \left\|\left[[H_0,\mu],H_0-\mu\bar{\varepsilon}\right]\right\|_{\mathcal{L}(L^2)}\ \forall s\in[0,\Delta t], \tag{29}$$

along with $\|\psi(t_j)\|_{L^2} = \|\psi_0\|_{L^2} = 1$, (21) and (25) we find that for all j,

$$\begin{aligned}
& \left\| i\dot{\varepsilon}(t_{j+\frac{1}{2}})\int_0^{\frac{1}{2}\Delta t}\int_{t_{j+\frac{1}{2}}-s}^{t_{j+\frac{1}{2}}+s} s(u-t_j)\tau(u-t_j)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\ duds\right\|_{L^2} \\
\leq \ & \left(\alpha_j+\mathcal{O}\left(\Delta t^2\right)\right)\int_0^{\frac{1}{2}\Delta t}\int_{t_{j+\frac{1}{2}}-s}^{t_{j+\frac{1}{2}}+s} s(u-t_j)\left\|\left[[H_0,\mu],H_0-\mu\bar{\varepsilon}\right]\right\|_{\mathcal{L}(L^2)}\|\psi(t_j)\|_{L^2}\ duds. \\
\leq \ & \frac{\alpha_j}{24}\left\|\left[[H_0,\mu],H_0-\mu\bar{\varepsilon}\right]\right\|_{\mathcal{L}(L^2)}\Delta t^4+\mathcal{O}\left(\Delta t^5\right).
\end{aligned}$$

We also prove easily that for all j,

$$\left\|S_j\left(\Delta t\right)[H_0,\mu]\psi(t_j)\mathcal{O}(\Delta t^6)\right\|_{L^2} = \mathcal{O}\left(\Delta t^6\right).$$

For the term of order 2, using (22), (24) and (20) and the first order expansion of φ_j around t_j, $\varphi_j(s)\psi = \varphi_j(t_j)\psi + (s-t_j)\theta(s-t_j)\psi$ for all $\psi \in L^2$, defining

$\theta : s \in [0, \Delta t] \mapsto \theta(s) \in \mathcal{L}(L^2)$, we can write

$$\begin{aligned}
& i\int_{t_j}^{t_{j+1}} \frac{1}{2}(s-t_{j+\frac{1}{2}})^2 \ddot{\varepsilon}(t_{j+\frac{1}{2}})\varphi_j(s)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\ ds \\
= \ & i\ddot{\varepsilon}(t_{j+\frac{1}{2}})\ \int_{t_j}^{t_{j+1}} \frac{1}{2}(s-t_{j+\frac{1}{2}})^2\left(\varphi_j(t_j)+(s-t_j)\theta(s-t_j)\right)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\ ds \\
= \ & \frac{i\ddot{\varepsilon}(t_{j+\frac{1}{2}})}{24} S_j\left(\Delta t\right)\mu\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\Delta t^3 \\
& + \frac{i\ddot{\varepsilon}(t_{j+\frac{1}{2}})}{2}\int_{t_j}^{t_{j+1}} (s-t_{j+\frac{1}{2}})^2(s-t_j)\theta(s-t_j)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\ ds \\
= \ & \frac{i\beta_j}{24} S_j\left(\Delta t\right)\mu\psi(t_j)\Delta t^3 + S_j\left(\Delta t\right)\mu\psi(t_j)\mathcal{O}(\Delta t^6) \\
& + \frac{i\ddot{\varepsilon}(t_{j+\frac{1}{2}})}{2}\int_{t_j}^{t_{j+1}} (s-t_{j+\frac{1}{2}})^2(s-t_j)\theta(s-t_j)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\ ds.
\end{aligned}$$

Using (20), we get the estimate $\|\theta(s)\|_{\mathcal{L}(L^2)} \leq \left\|\left[H_0,\mu\right]\right\|_{\mathcal{L}(L^2)}$, $\forall s \in [0,\Delta t]$, and using it with (22) and (25), we obtain that for all j,

$$\begin{aligned}
& \left\|\frac{i\ddot{\varepsilon}(t_{j+\frac{1}{2}})}{2}\int_{t_j}^{t_{j+1}} (s-t_{j+\frac{1}{2}})^2(s-t_j)\theta(s-t_j)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\ ds\right\|_{L^2} \\
\leq \ & \frac{1}{2}\left(\beta_j+\mathcal{O}\left(\Delta t^2\right)\right)\int_{t_j}^{t_{j+1}} (s-t_{j+\frac{1}{2}})^2(t_j-s)\left\|[H_0,\mu]\right\|_{\mathcal{L}(L^2)}\left\|\psi(t_j)\right\|_{L^2}\ ds \\
\leq \ & \frac{1}{2}\left(\beta_j+\mathcal{O}\left(\Delta t^2\right)\right)\left\|[H_0,\mu]\right\|_{\mathcal{L}(L^2)}\int_{-\frac{\Delta t}{2}}^{\frac{\Delta t}{2}} u^2\left(\frac{\Delta t}{2}-u\right)\ du \\
\leq \ & \frac{\beta_j}{48}\left\|[H_0,\mu]\right\|_{\mathcal{L}(L^2)}\Delta t^4 + \mathcal{O}\left(\Delta t^5\right).
\end{aligned}$$

and we also prove easily that $\left\|S_j\left(\Delta t\right)\mu\psi(t_j)\mathcal{O}(\Delta t^6)\right\|_{L^2} = \mathcal{O}\left(\Delta t^6\right)$.

Combining these results with (28) into equation (27), we obtain:

$$\begin{aligned}
\|Y(t_{j+1})\|_{L^2} &= \left\|\psi(t_{j+1}) - S_j(\Delta t)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\right\|_{L^2} \\
&\leq \left\|S_j(\Delta t)\left(\mathrm{Id}-\Omega^{\alpha_j}\Theta^{\beta_j}\right)\psi(t_j) + i\int_{t_j}^{t_{j+1}}\delta(s)\varphi_j(s)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\,ds\right\|_{L^2} \\
&\quad + \left\|i\int_{t_j}^{t_{j+1}} S_j(t_{j+1}-s)\delta(s)\mu Y(s)\,ds\right\|_{L^2} \\
&\leq \frac{1}{2}\|\mu\|^2_{\mathcal{L}(L^2)}\Delta\varepsilon\Delta t + \frac{\alpha_j}{24}\left\|\left[[H_0,\mu],H_0-\mu\bar{\varepsilon}\right]\right\|_{\mathcal{L}(L^2)}\Delta t^4 \\
&\quad + \frac{\beta_j}{48}\left\|[H_0,\mu]\right\|_{\mathcal{L}(L^2)}\Delta t^4 + \frac{1}{2}\|\mu\|^2_{\mathcal{L}(L^2)}\left(\Delta\varepsilon^2\Delta t^2 + \|\dot{\varepsilon}\|^2_{L^\infty(0,T)}\Delta t^4\right) \\
&\quad + \mathcal{O}(\Delta\varepsilon\Delta t^4) + \mathcal{O}(\Delta t^5)
\end{aligned}$$

We have now a local in time estimate that should be traduced in a global one, and from (26), we get

$$\begin{aligned}
&\|\psi(T)-\psi^{IK}(T)\|_{L^2}\\
\leq\ & (1+\mathcal{O}(\Delta t^2))\sum_{j=0}^{N-1}\left\|\psi(t_{j+1})-S_j(\Delta t)\Omega^{\alpha_j}\Theta^{\beta_j}\psi(t_j)\right\|_{L^2}\\
\leq\ & \frac{T}{2}\|\mu\|^2_{\mathcal{L}(L^2)}\Delta\varepsilon+\frac{\alpha_j T}{24}\left\|\left[[H_0,\mu],H_0-\mu\bar{\varepsilon}\right]\right\|_{\mathcal{L}(L^2)}\Delta t^3\\
&+\frac{\beta_j T}{48}\left\|[H_0,\mu]\right\|_{\mathcal{L}(L^2)}\Delta t^3+\frac{T}{2}\|\mu\|^2_{\mathcal{L}(L^2)}\left(\Delta\varepsilon^2\Delta t+\|\dot{\varepsilon}\|^2_{L^\infty(0,T)}\Delta t^3\right)\\
&+\mathcal{O}(\Delta\varepsilon\Delta t^3)+\mathcal{O}(\Delta t^4).
\end{aligned}$$

The result follows, with

$$\lambda_1'=\frac{T}{2}\|\mu\|^2_{\mathcal{L}(L^2)}(1+\Delta\varepsilon\Delta t)$$

and

$$\lambda_2'=\frac{\alpha_j T}{24}\left\|\left[[H_0,\mu],H_0-\mu\bar{\varepsilon}\right]\right\|_{\mathcal{L}(L^2)}+\frac{\beta_j T}{48}\left\|[H_0,\mu]\right\|_{\mathcal{L}(L^2)}+\frac{T}{2}\|\mu\|^2_{\mathcal{L}(L^2)}\|\dot{\varepsilon}\|^2_{L^\infty(0,T)}$$

□

In this theorem, the constants λ_2' depends on $\|\varepsilon\|_{L^\infty(0,T)}$ through the commutator $\left[[H_0,\mu],H_0-\mu\bar{\varepsilon}\right]$ that appears in (29). This contrasts with the result obtained in Theorem 2. The explanation of this situation comes from the fact that the norms of $\varphi_j(s):=S_j(t_{j+1}-s)\mu S_j(s-t_j)$ (defined in (17)) and its first derivative does not depend on $\|\varepsilon\|_{L^\infty(0,T)}$, whereas its second derivative does. Thus, errors in Algorithm 2 depend on L^∞-norm of the control field as in the case of the second order Strang operator splitting. Although these two methods present the same computational complexity, the order of Algorithm 2 is higher when $\Delta\varepsilon$ scales Δt^3.

5. Improvement in the limit of large intensities

We now describe a way to improve the time order of the Algorithm 1 in the case of large intensities. The following method enables to replace $\Delta\varepsilon$ by $\Delta\varepsilon\Delta t$ in the estimates.

5.1. **Algorithm.**

The algorithm we propose improve the accuracy in the approximation of ε. This improvement is obtained by using two toolkit elements instead of one at each time step.

Algorithm 3. *(Improved toolkit method for large intensities)*

(1) *Preprocessing. Precompute the "toolkit", i.e. the set of propagators:*

$$S_\ell(\Delta t)\text{ for }\ell=0,\cdots,m,$$

where $(S_\ell(t))_{t\in\mathbb{R}}$ denotes the one-parameter group generated by the operator $H_0-\mu\bar{\varepsilon}_\ell$, the sequence $(\varepsilon_\ell)_{\ell=0,\cdots,m,}$ being defined by (4).

(2) *Given a control field $\varepsilon\in L^\infty$ satisfying $\mathcal{H}$ and $\psi_0^{JK}=\psi_0$, the sequence $(\psi_j^{JK})_{j=0,\ldots,N}$ that approximates $(\psi(t_j))_{j=0,\ldots,N}$, is obtained recursively by iterating the following loop:*

(a) *Find* ℓ_j *such that:*

$$\varepsilon(t_{j+1/2}) \in [\bar{\varepsilon}_{\ell_j}, \bar{\varepsilon}_{\ell_j+1}].$$

(b) *Compute* α_j *and* β_j *such that:*

$$\begin{aligned} \alpha_j \bar{\varepsilon}_{\ell_j} + \beta_j \bar{\varepsilon}_{\ell_j+1} &= \varepsilon(t_{j+1/2}) \\ \alpha_j + \beta_j &= 1 \end{aligned} \tag{30}$$

(c) *Set* $\psi^{JK}_{j+1} = S_{\ell_j+1}(\Delta t)^{\beta_j} S_{\ell_j}(\Delta t)^{\alpha_j} \psi^{JK}_j$.

In this method, one must perform two online matrices exponentiations. The cost of the corresponding step, namely Step *2c* can be reduced to three matrix products when precomputing the mappings between the diagonalization basis of two consecutive toolkit elements.

Remark 4. *Another way to reduce the cost of this step, is to quantify the values of* α_j *(and* β_j*) and precompute a toolkit containing elements of the form :* $S_{\ell_j+1}(\Delta t)^{\beta_j} S_{\ell_j}(\Delta t)^{\alpha_j}$. *This method is tested in Sec. 6.*

5.2. **Analysis of the method.** We can now repeat the analysis that has been done in the proof of Theorem 2 to obtain the following estimate.

Theorem 4. *Let* $\varepsilon \in W^{3,\infty}(0,T)$, ψ *be the corresponding solution of* (2) *and* ψ^{JK} *the approximation of* ψ *obtained with Algorithm 2. Given* $\Delta t > 0$ *and* $\Delta\varepsilon > 0$, *there exists* $\lambda_1'' > 0$, $\lambda_2'' > 0$, *both independent of* $\|\varepsilon\|_{L^\infty(0,T)}$ *such that:*

$$\|\psi(T) - \psi^{JK}(T)\|_{L^2} \leq \lambda_1'' \Delta\varepsilon \Delta t + \lambda_2'' \Delta t^2.$$

Proof. In this algorithm, two control fields are involved successively in the propagation over the interval $[t_j, t_{j+1}]$. As in the previous proofs, we introduce $\delta(s) = \varepsilon(s) - \bar{\varepsilon}(s)$, with

$$\bar{\varepsilon}(s) = \begin{cases} \bar{\varepsilon}_{\ell_j} & s \in [t_j, t_j + \alpha_j \Delta t[, \\ \bar{\varepsilon}_{\ell_j+1} & s \in [t_j + \alpha_j \Delta t, t_{j+1}[. \end{cases}$$

Note first that for all $s \in [t_j, t_{j+1}]$

$$|\delta(s)| \leq \Delta\varepsilon + \frac{1}{2} \|\dot{\varepsilon}\|_{L^\infty(0,T)} \Delta t \tag{31}$$

and denote by $(S_j(t))_{j=0,\dots,N-1}$ and $\left(S'_j(t)\right)_{j=0,\dots,N-1}$ the one-parameter semigroups generated by the operators $H_0 - \mu\bar{\varepsilon}_{\ell_j}$ and $H_0 - \mu\bar{\varepsilon}_{\ell_j+1}$ respectively.
Following the same analysis as for Algorithm 1, we set $(\psi^{JK}_j)_{j=0,\dots,N}$ as the time discretization of the solution of:

$$\begin{cases} i\partial_t \psi^{JK}(t) = \left(H_0 - \mu\bar{\varepsilon}(t)\right) \psi^{JK}(t), & \mathbb{R}^3 \times (0,T) \\ \psi^{JK}(0) = \psi_0, & \mathbb{R}^3 \end{cases} \tag{32}$$

where $\bar{\varepsilon}(t)$ (defined right above) is constant over each interval $[t_j, t_j + \alpha_j \Delta t[$ and $[t_j + \alpha_j \Delta t, t_{j+1}[$, with $j = 0, ..., N-1$. In the same way as we obtained (8), the solution ψ of (2) satisfies,

$$\psi(t_j + \alpha_j \Delta t) = S_j(\alpha_j \Delta t)\psi(t_j) - i \int_{t_j}^{t_j + \alpha_j \Delta t} S_j(t_j + \alpha_j \Delta t - s) \mu \delta(s) \psi(s)\, ds$$

and

$$\psi(t_{j+1}) = S'_j(\beta_j\Delta t)\psi(t_j+\alpha_j\Delta t) - i\int_{t_j+\alpha_j\Delta t}^{t_{j+1}} S'_j(t_{j+1}-s)\mu\delta(s)\psi(s)\ ds.$$

As in (12), it gives rise to:

$$\begin{aligned}
&\psi(t_{j+1}) - S'_j(\beta_j\Delta t)S_j(\alpha_j\Delta t)\psi(t_j)\\
=\ & i\int_{t_j+\alpha_j\Delta t}^{t_{j+1}} S'_j(t_{j+1}-s)\mu\delta(s)\psi(s)\ ds\\
&+i\int_{t_j}^{t_j+\alpha_j\Delta t} S'_j(\beta_j\Delta t)S_j(t_j+\alpha_j\Delta t-s)\mu\delta(s)\psi(s)\ ds\\
=\ & i\int_{t_j+\alpha_j\Delta t}^{t_{j+1}} S'_j(t_{j+1}-s)\mu\delta(s)\left(\psi(s) - S'_j(s-t_j-\alpha_j\Delta t)\psi(t_j+\alpha_j\Delta t)\right)\ ds\\
&+i\int_{t_j}^{t_j+\alpha_j\Delta t} S'_j(\beta_j\Delta t)S_j(t_j+\alpha_j\Delta t-s)\mu\delta(s)\left(\psi(s) - S_j(s-t_j)\psi(t_j)\right)\ ds\\
&+i\int_{t_j+\alpha_j\Delta t}^{t_{j+1}} \delta(s)\widetilde{\varphi}'_j(s)S_j(\alpha_j\Delta t)\psi(t_j)\ ds\\
&+i\int_{t_j}^{t_j+\alpha_j\Delta t} S'_j(\beta_j\Delta t)\delta(s)\widetilde{\varphi}_j(s)\psi(t_j)\ ds. \qquad (33)
\end{aligned}$$

where $\widetilde{\varphi}'_j(s) := S'_j(t_{j+1}-s)\mu S'_j(s-t_j-\alpha_j\Delta t)$ and $\widetilde{\varphi}_j(s) := S_j(t_j+\alpha_j\Delta t-s)\mu S_j(s-t_j)$. As in the proof of Theorem 2 (see right above (11)) we use the appropriate decomposition

$$\begin{aligned}
\psi(T) - \psi^{JK}(T) &= \psi(T) - S'_{N-1}(\beta_{N-1}\Delta t)S_{N-1}(\alpha_{N-1}\Delta t)\psi(t_{N-1})\\
&+ \sum_{j=0}^{N-2} S'_{N-1}(\beta_{N-1}\Delta t)S_{N-1}(\alpha_{N-1}\Delta t)\dots S'_{j+1}(\beta_{j+1}\Delta t)S_{j+1}(\alpha_{j+1}\Delta t)\\
&\qquad\qquad \times\left(\psi(t_{j+1}) - S'_j(\beta_j\Delta t)S_j(\alpha_j\Delta t)\psi(t_j)\right)\\
&+ S'_{N-1}(\beta_{N-1}\Delta t)S_{N-1}(\alpha_{N-1}\Delta t)\dots S'_0(\beta_0\Delta t)S_0(\alpha_0\Delta t)\psi_0 - \psi^{JK}(T)
\end{aligned}$$

where the last line is equal to 0 since ψ^{JK} satisfies (32) on $[0,T]$. We have the corresponding estimate (see (11))

$$\|\psi(T) - \psi^{JK}(T)\|_{L^2} \le \sum_{j=0}^{N-1} \left\|\psi(t_{j+1}) - S'_j(\beta_j\Delta t)S_j(\alpha_j\Delta t)\psi(t_j)\right\|_{L^2}$$

and we will thus calculate and estimate in L^2-norm for all j the four terms of (33). As in (15), but using now the new estimate (31) of δ, the two first terms of the right hand side of (33) can be respectively estimated by:

$$\begin{aligned}
&\left\| i\int_{t_j+\alpha_j\Delta t}^{t_{j+1}} S'_j(t_{j+1}-s)\mu\delta(s)\left(\psi(s) - S'_j(s-t_j-\alpha_j\Delta t)\psi(t_j+\alpha_j\Delta t)\right)\ ds\right\|_{L^2}\\
&\qquad\le\ \beta_j\|\mu\|^2_{\mathcal{L}(L^2)}\left(\Delta\varepsilon^2\Delta t^2 + \frac{1}{2}\|\dot{\varepsilon}\|^2_{L^\infty(0,T)}\Delta t^4\right) \qquad (34)
\end{aligned}$$

and

$$\left\| i\int_{t_j}^{t_j+\alpha_j\Delta t} S_j'(\beta_j\Delta t)S_j(t_j+\alpha_j\Delta t-s)\mu\delta(s)\left(\psi(s)-S_j(s-t_j)\psi(t_j)\right)\right\|_{L^2} \leq \alpha_j\|\mu\|^2_{\mathcal{L}(L^2)}\left(\Delta\varepsilon^2\Delta t^2+\frac{1}{2}\|\dot\varepsilon\|^2_{L^\infty(0,T)}\Delta t^4\right). \tag{35}$$

Let us now focus on the third and fourth terms of (33). We have:

$$\begin{aligned}\int_{t_j+\alpha_j\Delta t}^{t_{j+1}}\delta(s)\widetilde\varphi_j'(s)S_j(\alpha_j\Delta t)\psi(t_j)\,ds &= \int_{t_j+\alpha_j\Delta t}^{t_{j+1}}\delta(s)\widetilde\varphi_j'(t_j+\alpha_j\Delta t)S_j(\alpha_j\Delta t)\psi(t_j)\,ds\\ &+\int_{t_j+\alpha_j\Delta t}^{t_{j+1}}\delta(s)\int_{t_j+\alpha_j\Delta t}^{s}\partial_u\widetilde\varphi_j'(u)\,du\;S_j(\alpha_j\Delta t)\psi(t_j)\,ds\\ &=\int_{t_j+\alpha_j\Delta t}^{t_{j+1}}\delta(s)S_j'(\beta_j\Delta t)\mu S_j(\alpha_j\Delta t)\psi(t_j)\,ds\\ &+\int_{t_j+\alpha_j\Delta t}^{t_{j+1}}\delta(s)\int_{t_j+\alpha_j\Delta t}^{s}\partial_u\widetilde\varphi_j'(u)\,du\;S_j(\alpha_j\Delta t)\psi(t_j)\,ds\end{aligned}$$

and

$$\begin{aligned}\int_{t_j}^{t_j+\alpha_j\Delta t}S_j'(\beta_j\Delta t)\delta(s)\widetilde\varphi_j(s)\psi(t_j)\,ds &= \int_{t_j}^{t_j+\alpha_j\Delta t}\delta(s)S_j'(\beta_j\Delta t)\widetilde\varphi_j(t_j+\alpha_j\Delta t)\psi(t_j)\,ds\\ &-\int_{t_j}^{t_j+\alpha_j\Delta t}\delta(s)S_j'(\beta_j\Delta t)\int_{s}^{t_j+\alpha_j\Delta t}\partial_u\widetilde\varphi_j(u)\,du\;\psi(t_j)\,ds\\ &=\int_{t_j}^{t_j+\alpha_j\Delta t}\delta(s)S_j'(\beta_j\Delta t)\mu S_j(\alpha_j\Delta t)\psi(t_j)\,ds\\ &-\int_{t_j}^{t_j+\alpha_j\Delta t}\delta(s)S_j'(\beta_j\Delta t)\int_{s}^{t_j+\alpha_j\Delta t}\partial_u\widetilde\varphi_j(u)\,du\;\psi(t_j)\,ds.\end{aligned}$$

By means of (30), we have:

$$\begin{aligned}\int_{t_j}^{t_{j+1}}\delta(s)\,ds &= \int_{t_j}^{t_{j+1}}\varepsilon(s)-\varepsilon(t_{j+1/2})\,ds+\int_{t_j}^{t_{j+1}}\varepsilon(t_{j+1/2})-\bar\varepsilon(s)\,ds\\ &=\int_{t_j}^{t_{j+1}}\varepsilon(s)-\varepsilon(t_{j+1/2})\,ds\\ &=\int_{t_j}^{t_{j+1}}\ddot\varepsilon(\theta(s))\frac{1}{2}(s-t_{j+1/2})^2\,ds,\end{aligned}$$

where $\theta(s)\in[t_j,t_{j+1}]$. Consequently,

$$\left\|\int_{t_j}^{t_{j+1}}\delta(s)S_j'(\beta_j\Delta t)\mu S_j(\alpha_j\Delta t)\psi(t_j)\,ds\right\|_{L^2}\leq\frac{1}{24}\|\mu\|_{\mathcal{L}(L^2)}\|\ddot\varepsilon\|_{L^\infty(0,T)}\Delta t^3. \tag{36}$$

From (20) and (31), we obtain

$$\left\| \int_{t_j+\alpha_j\Delta t}^{t_{j+1}} \delta(s) \int_{t_j+\alpha_j\Delta t}^{s} \partial_u \widetilde{\varphi}_j'(u)\ du\ S_j(\alpha_j\Delta t)\psi(t_j)\ ds \right\|_{L^2} \leq \frac{1}{2}\beta_j^2 \|[H_0,\mu]\|_{\mathcal{L}(L^2)} \left(\Delta\varepsilon + \frac{1}{2}\|\dot{\varepsilon}\|_{L^\infty(0,T)}\Delta t\right)\Delta t^2 \tag{37}$$

and similarly, we find that:

$$\left\| \int_{t_j}^{t_j+\alpha_j\Delta t} \delta(s) S_j'(\beta_j\Delta t) \int_{s}^{t_j+\alpha_j\Delta t} \partial_u \widetilde{\varphi}_j(u)\ du\ \psi(t_j)\ ds \right\|_{L^2} \leq \frac{1}{2}\alpha_j^2 \|[H_0,\mu]\|_{\mathcal{L}(L^2)} \left(\Delta\varepsilon + \frac{1}{2}\|\dot{\varepsilon}\|_{L^\infty(0,T)}\Delta t\right)\Delta t^2. \tag{38}$$

Combining (34), (35), (36), (37) and (38), we obtain:

$$\begin{aligned} \left\|\psi(t_{j+1}) - S_j'(\beta_j\Delta t)S_j(\alpha_j\Delta t)\psi(t_j)\right\|_{L^2} \leq\ & \|\mu\|_{\mathcal{L}(L^2)}^2 \left(\Delta\varepsilon^2 + \frac{1}{2}\|\dot{\varepsilon}\|_{L^\infty(0,T)}^2\Delta t^2\right)\Delta t^2 \\ & + \frac{1}{24}\|\mu\|_{\mathcal{L}(L^2)}\|\ddot{\varepsilon}\|_{L^\infty(0,T)}\Delta t^3 \\ & + \frac{1}{2}\|[H_0,\mu]\|_{\mathcal{L}(L^2)} \left(\Delta\varepsilon + \frac{1}{2}\|\dot{\varepsilon}\|_{L^\infty(0,T)}\Delta t\right)\Delta t^2. \end{aligned}$$

The global estimate follows

$$\begin{aligned} \|\psi(T) - \psi^{JK}(T)\|_{L^2} \leq\ & \sum_{j=0}^{N-1} \left\|\psi(t_{j+1}) - S_j'(\beta_j\Delta t)S_j(\alpha_j\Delta t)\psi(t_j)\right\|_{L^2} \\ \leq\ & \|\mu\|_{\mathcal{L}(L^2)}^2 \left(\Delta\varepsilon^2 + \frac{1}{2}\|\dot{\varepsilon}\|_{L^\infty(0,T)}^2\Delta t^2\right) T\Delta t \\ & + \frac{1}{24}\|\mu\|_{\mathcal{L}(L^2)}\|\ddot{\varepsilon}\|_{L^\infty(0,T)} T\Delta t^2 \\ & + \frac{1}{2}\|[H_0,\mu]\|_{\mathcal{L}(L^2)} \left(\Delta\varepsilon + \frac{1}{2}\|\dot{\varepsilon}\|_{L^\infty(0,T)}\Delta t\right) T\Delta t \end{aligned}$$

and the proof of Theorem 4 is complete, with

$$\lambda_1'' = \frac{1}{2}\|[H_0,\mu]\|_{\mathcal{L}(L^2)}T + \|\mu\|_{\mathcal{L}(L^2)}^2 T\Delta\varepsilon,$$

$$\begin{aligned} \lambda_2'' =\ & \frac{1}{4}\|[H_0,\mu]\|_{\mathcal{L}(L^2)}\|\dot{\varepsilon}\|_{L^\infty(0,T)}T + \frac{1}{24}\|\mu\|_{\mathcal{L}(L^2)}\|\ddot{\varepsilon}\|_{L^\infty(0,T)}T \\ & + \frac{1}{2}\|\mu\|_{\mathcal{L}(L^2)}^2\|\dot{\varepsilon}\|_{L^\infty(0,T)}T\Delta t. \end{aligned}$$

□

6. Numerical results

In this section, we check numerically that the order of the estimates we have obtained in this paper are optimal, and we compare computational costs of the methods.

6.1. **Model.** In order to test the performance of the algorithms on a realistic case, a model already treated in the literature has been considered. The system is a molecule of HCN modeled as a rigid rotator. We refer the reader to [15] for numerical details concerning this system.
As a control field, we use an arbitrary field of the form $\varepsilon(t) = \varepsilon_{\max}\sin(\omega t)$, with $\varepsilon_{\max} = 5.10^{-5}$ and $\omega = 5.10^{-6}$. The parameters are chosen in accordance with usual scales considered for this model. The use of an analytic formula for the field enables us to work with exact values, i.e. to test the cases $\Delta\varepsilon = 0$.

6.2. **Orders of convergence.** To test the time order, we first work with $\Delta\varepsilon = 0$, with various values of Δt. The numerical orders correspond to the ones obtained in our analysis. Curves of convergence are depicted in Fig. 1.

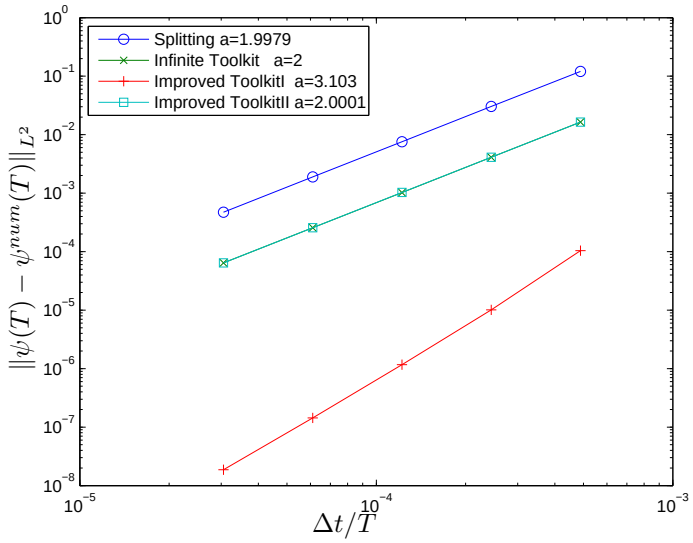

FIGURE 1. Error with respect to Δt, when $\Delta\varepsilon = 0$ for toolkit method and Improved toolkit I method, and when$\Delta\varepsilon = c\Delta t$ for Improved toolkit II method. Here, ψ^{num} stands for the approximation of ψ when using the toolkit method, the second order Strang operator splitting, the Improved toolkit I method and the Improved toolkit II. The coefficient a is the regression coefficient.

The order with respect to $\Delta\varepsilon$ is also obtained numerically by using a small time step. In this test, the numerical order is consistent with the one obtained in Theorem 2. The convergence with respect to this parameter is presented in Fig. 2.

6.3. **Computational cost.** In a second test, we compare the computational costs of the methods. To do this, we look for the values of $N = \frac{T}{\Delta t}$ and $m = \frac{\varepsilon_{\max}}{\Delta\varepsilon}$ that enable to reach a fixed arbitrary error of $Tol = 5.10^{-3}$ (recall that in any case the error cannot exceed 2). For sake of simplicity, we only test powers of 2. In this test, we also include the quantified version of the Improved toolkit II which is described

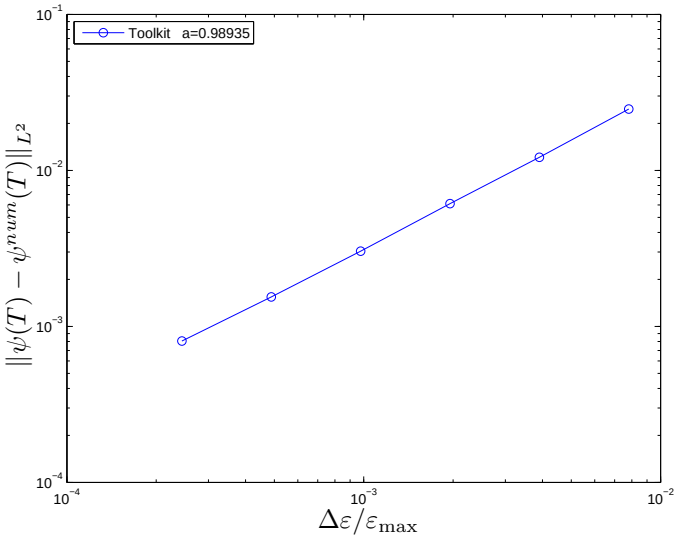

FIGURE 2. Error with respect to $\Delta\varepsilon$, when Δt is small. Here, ψ^{num} stands for the approximation of ψ when using the toolkit method.

in Remark 4. In our case, the parameters α and β were quantified among 100 values uniformly distributed in $[0, 1]$.

	$N = \frac{T}{\Delta t}$	Matrix products	$m = \frac{\varepsilon_{\max}}{\Delta\varepsilon}$
Strang Op. Splitting	16384	32768	-
Toolkit	8192	8192	16384
Improved toolkit I	1024	2048	16384
Improved toolkit II	4096	12288	16
Quantified Improved toolkit II	4096	4096	6400

TABLE 1. Values of numerical parameters corresponding to a tolerance error of $Tol = 5.10^{-3}$.

These tests show that toolkit methods always give better results as the second order Strang operator splitting.
The two improvements we propose in this paper enable to reduce respectively the global number of matrix products and the size of the toolkit, which is in agreement with the analysis we have done. Note that the second improvement reduce significantly preprocessing step. This fact makes feasible the quantified version of it, which requires intrinsically a larger toolkit.

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References

[1] A. Assion, T. Baumert, M. Bergt, T. Brixner, B. Kiefer, V. Seyfried, M. Strehle, and G. Gerber, *Control of chemical reactions by feedback-optimized phase-shaped femtosecond laser pulses*, Science, 282 (1998), pp. 919–922.

[2] G. Balint-Kurti, F. Manby, Q. Ren, M. Artamonov, T. Ho, and H. Rabitz, *Quantum control of molecular motion including electronic polarization effects with a two-stage toolkit*, J. Chem. Phys., 122 (2005).

[3] M. Belhadj, J. Salomon, and G. Turinici, *Monotonic time-discretized schemes in quantum controlMonotonic time-discretized schemes in quantum control, journal = J. Phys. A, year = 2008, volume = 41, number = , pages = 362001-362011, optnote = DOI: 10.1088/1751-8113/41/36/362001.*

[4] C. Besse, B. Bidégaray, and S. Descombes, *Order estimates in time of splitting methods for the nonlinear Schrödinger equation*, SIAM J. Numer. Anal., 40 (2002), pp. 26–40 (electronic).

[5] H. Brezis, *Analyse fonctionnelle : Thorie et applications*, Dunod, 1994.

[6] T. Cazenave and A. Haraux, *An Introduction to Semilinear Evolution Equations*, Oxford University, 1998.

[7] I. L. Chuang, R. Laflamme, P. W. Shor, and W. H. Zurek, *Quantum computers, factoring, and decoherence*, Science, 270 (1995), pp. 1633–1635.

[8] P. G. Ciarlet and J. L. Lions, eds., *Handbook of numerical analysis. Vol. IX*, Handbook of Numerical Analysis, IX, North-Holland, Amsterdam, 2003. Numerical methods for fluids. Part 3.

[9] T. Jahnke and C. Lubich, *Error bounds for exponential operator splittings*, BIT, 40 (2000), pp. 735–744.

[10] R. Judson and H. Rabitz, *Teaching lasers to control molecules*, Phys. Rev. Lett, 68 (1992), p. 1500.

[11] R. J. Levis, G. Menkir, and H. Rabitz, *Selective bond dissociation and rearrangement with optimally tailored, strong-field laser pulses*, Science, 292 (2001), pp. 709–713.

[12] H. Rabitz, R. de Vivie-Riedle, M. Motzkus, and K. Kompa, *Wither the future of controlling quantum phenomena?*, Science, 288 (2000), pp. 824–828.

[13] H. Rabitz, G. Turinici, and E. Brown, *Control of quantum dynamics: Concepts, procedures and future prospects*, in Computational Chemistry, Special Volume (C. Le Bris Editor) of Handbook of Numerical Analysis, vol X, P. G. Ciarlet, ed., Elsevier Science B.V., 2003, pp. 833–887.

[14] M. Reed and B. Simon, *Methods of Modern Mathematical Physics, II, Fourier analysis, self-adjointness*, Academic Press, 1975.

[15] J. Salomon, C. Dion, and G. Turinici, *Optimal molecular alignment and orientation through rotational ladder climbing*, J. Chem. Phys., 123 (2005), p. 144310.

[16] J. M. Sanz-Serna and J. G. Verwer, *Conservative and nonconservative schemes for the solution of the nonlinear Schrödinger equation*, IMA J. Numer. Anal., 6 (1986), pp. 25–42.

[17] K. Sayood, *Introduction to data compression, 3^{rd} edition*, Morgan Kaufmann, Elsevier., 2006.

[18] G. Strang, *On the construction and comparison of difference schemes*, SIAM J. Numer. Anal., 5 (1968), pp. 506–517.

[19] W. Warren, H. Rabitz, and M. Dahleh, *Coherent control of quantum dynamics: The dream is alive*, Science, 259 (1993), pp. 1581–1589.

[20] T. Weinacht, J. Ahn, and P. Bucksbaum, *Controlling the shape of a quantum wavefunction*, Nature, 397 (1999), pp. 233–235.

[21] F. Yip, D. Mazziotti, and H. Rabitz, *A local-time algorithm for achieving quantum control*, J. Phys. Chem. A., 107 (2003), pp. 7264–7269.

[22] ———, *A propagation toolkit to design quantum control*, J. Chem. Phys., 118(18) (2003), pp. 8168–8172.