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# Splitting Methods for the Time-dependent Schrödinger Equation

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**Abstract**

Cheap and easy to implement fourth-order methods for the Schrödinger equation with time-dependent Hamiltonians are introduced. The methods require evaluations of exponentials of simple unidimensional integrals, and can be considered an averaging technique, preserving many of the qualitative properties of the exact solution.

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**INTRODUCTION**. In this work we present new fourth-order geometric integrators for solving the time-dependent Schrödinger equation ($\hbar = 1$)

$$i\frac{d}{dt}\psi(x,t) = \hat{H}(p,x,t)\psi(x,t) \qquad\qquad \psi(x,0) = \psi_0(x) \tag{1}$$

where $\psi(x,t)$ is the wave function associated with the system, $p \equiv -i\frac{\partial}{\partial x}$ and $\hat{H}(p,x,t)$ is a Hermitian Hamiltonian operator governing the evolution of the system. Some standard techniques are found in the literature for solving (1) as a linear ordinary differential equation:

*(i)* - Spatial discretisation of $\psi(x,t)$. Let us assume that the system is defined in the interval $x \in [x_0, x_f]$. We can then split this interval in $N$ parts

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of length $\triangle x = (x_f - x_0)/N$ and consider $c_n = \psi(x_n, t)$ where $x_n = x_0 + n\ \triangle x$, $n = 1, \ldots, N$, thus obtaining the finite dimensional linear equation

$$i\,\frac{d}{dt}\mathbf{c}(t) = \mathbf{H}(t)\mathbf{c}(t) \qquad\qquad \mathbf{c}(0) = \mathbf{c}_0, \tag{2}$$

where $\mathbf{c} = (c_1, \ldots, c_N)^T \in \mathbb{C}^N$ and $\mathbf{H} \in \mathbb{C}^{N\times N}$ is an Hermitian matrix associated to the Hamiltonian (usually it is real and symmetric).

If the Hamiltonian takes the form $\hat{H} = \hat{T}(p,t) + \hat{V}(x,t)$, then $\hat{V}$ is diagonal in the coordinate space and $\hat{T}$ is diagonal in momentum space. We can use complex Fast Fourier Transforms (FFTs) for evaluating it as $\hat{T}\psi(x_n, t) = \mathcal{F}^{-1} D_T \mathcal{F} \psi(x_n, t)$, where $D_T$ is a diagonal operator. Also finite difference methods produce similar finite dimensional systems, but in this case the spatial accuracy is reduced.

*(ii)* - <u>Spectral decomposition</u>. Let us suppose the solution of (1) can be approximated by

$$\psi(x,t) \simeq \sum_{n=0}^{N} c_n(t) e^{-itE_n} \psi_n(x) \tag{3}$$

where $E_n$ and $\psi_n$ are the exact eigenvalues and eigenfunctions of a time-independent Hamiltonian, $\hat{H}_0$, e.g. a Harmonic oscillator, and the complex coefficients $c_n$ give the probability amplitude to find the system in the state $\psi_n$. Then, substituting (3) into (1) we obtain a matricial equation similar to (2) for this basis, with $\mathbf{c} = (c_1, \ldots, c_N)$ and $(\mathbf{H}(t))_{ij} = \langle \psi_i | \hat{H}(t) - \hat{H}_0 | \psi_j \rangle e^{i(E_i - E_j)t}$, $i, j = 1, \ldots, N$, where the standard bracket notation is used.

In the following we will present new numerical methods of fourth-order (in the time-step $\tau$) for solving (2). They will be written in terms of exponentials of linear combinations of $\int_0^\tau \mathbf{H}(t)\,dt$ and $\int_0^\tau t\,\mathbf{H}(t)\,dt$, preserving many of the qualitative properties of the exact solution. After this averaging of the time-dependent part of the Hamiltonian, the system can be considered as autonomous. So standard techniques like splitting methods can be used for evaluating the exponentials. To avoid the need for complex number computations, we apply the fact that the quantum system (2) is equivalent to a $2N$ degree of freedom classical Hamiltonian system. Finally the performance of the methods is illustrated with several examples.

**SECOND AND FOURTH-ORDER METHODS** If $\mathbf{H}$ is a constant matrix, the Schrödinger equation has the solution

$$\mathbf{c}(t) = \mathbf{U}(t,0)\mathbf{c}(0) = \exp\left(-it\mathbf{H}\right)\mathbf{c}(0), \tag{4}$$

where $\mathbf{U}$ is the unitary evolution operator. For this problem, a number of methods have been developed. The optimal method varies for each specific problem (depending on the structure of $\mathbf{H}$, how frequently output is desired, etc. [1]). In most cases the geometric integrators frequently used in the context of classical mechanics [2] can be used to solve (4), preserving some qualitative properties (symplecticity, unitarity, time-symmetry, etc.)[3, 4]. In conclusion, high-order and very efficient methods have been developed for numerically evaluating (4).

If the Hamiltonian is explicitly time-dependent, the situation is different. The unitary evolution operator has to satisfy the equation $i\dot{\mathbf{U}} = \mathbf{H}(t)\mathbf{U}$ and the exact solution can formally be written as

$$\mathbf{U}(t,0) = \mathcal{T}e^{\left(-i\int_0^t \mathbf{H}(s)ds\right)}$$

where $\mathcal{T}$ is the standard time ordering operator which gives rise to more complicated expressions to disentangle. If $\int_0^t [\mathbf{H}(t),\mathbf{H}(s)]\,ds = 0, \ \ \forall t > 0$, where $[\mathbf{A},\mathbf{B}] = \mathbf{AB} - \mathbf{BA}$, the solution is given by $\mathbf{U}(t,0) = \exp\left(-i\int_0^t \mathbf{H}(s)ds\right)$. This is not the usual case and in general one has to look for numerical approximate solutions.

If we split the interval $(0,t)$ into $N_t$ subintervals then

$$\mathbf{U}(t,0) = \prod_{n=0}^{N_t-1} \mathbf{U}(t_n+\tau, t_n)$$

with $\tau = t/N_t$ and $t_n = n\tau$. If $\tau$ is sufficiently small and $\mathbf{H}(t)$ is a bounded matrix, each step can be written in exponential form $\mathbf{U}(t_n+\tau,t_n) = e^{\Omega(t_n+\tau,t_n)}$, where $\Omega = \sum_{n=1}^{\infty}\Omega_n$ is the Magnus series [5, 6]. The first two terms are given by

$$\Omega_1 = -i\int_{t_n}^{t_n+\tau} \mathbf{H}(\tau_1)d\tau_1 \tag{5}$$

$$\Omega_2 = -\frac{1}{2}\int_{t_n}^{t_n+\tau}\int_{t_n}^{\tau_1} [\mathbf{H}(\tau_1),\mathbf{H}(\tau_2)]d\tau_2\,d\tau_1, \tag{6}$$

and it is well known that $\exp(\Omega_1)$ provides a second order approximation. Then, if the Hamiltonian is separable in the form

$$\mathbf{H}(p,x,t) = \mathbf{T}(p,t) + \mathbf{V}(x,t) \tag{7}$$

where $\mathbf{T}$ and $\mathbf{V}$ are the matrices associated with kinetic and potential energy respectively, we can evaluate (5) using different second order quadratures (midpoint, trapezoidal, etc.), e.g. a staggered grid

$$\Omega_1(t) = \tau \mathbf{T}_{1/2} + \frac{\tau}{2}(\mathbf{V}_0 + \mathbf{V}_1) + O(\tau^3) \tag{8}$$

with $\mathbf{T}_{1/2} = -i\mathbf{T}(t_n + \frac{\tau}{2})$ and $\mathbf{V}_k = -i\mathbf{V}(t_n + k\tau)$, $\quad k = 0, 1$, and we can use second order splitting methods in several forms, e.g.

$$\mathbf{U} = e^{\Omega_1} + O(\tau^3) = e^{\frac{\tau}{2}\mathbf{V}_1}\, e^{\tau \mathbf{T}_{1/2}}\, e^{\frac{\tau}{2}\mathbf{V}_0} + O(\tau^3), \tag{9}$$

belonging to the family of standard second order splitting methods widely analysed in the literature (known as leap-frog, Störmer or Verlet). In order to see that the error is effectively of order $O(\tau^3)$ we can utilise the BCH formula. The first error term of (9) is proportional to $\tau^2[\mathbf{T}_{1/2}, \mathbf{V}_1 - \mathbf{V}_0]$, but $\mathbf{V}_1 - \mathbf{V}_0 = O(\tau)$ if we assume sufficient smoothness of $\mathbf{V}(x,t)$. Similar methods to (8) and (9) can be obtained by interchanging $\mathbf{T}$ and $\mathbf{V}$. If $\mathbf{T}$ and $\mathbf{V}$ share the same time-dependent functions, it may be convenient to evaluate both using the same quadrature (in order to evaluate the functions at the same points).

Observe that, if no output is desired, (9) necessitates only one time-dependent evaluation of $\mathbf{V}(x,t)$ and $\mathbf{T}(p,t)$ per step (a FSAL property). The matrices $\exp(\mathbf{V})$ are diagonal in the configuration space while $\exp(\mathbf{T})$ are diagonal in the momentum space. So complex FFTs can be used, requiring only $O(N \log N)$ floating point operations to transform between these spaces.

These methods are cheap, easy to implement, have good stability properties and preserve many of the qualitative properties of the exact solution. The main problem is low accuracy. To obtain higher order methods while preserving these important properties is a more complicated task than in the case of constant Hamiltonians. Different methods have appeared for solving this problem [7, 8, 9, 10, 11], but they usually are difficult to implement, are expensive or can be used only under very special conditions on the Hamiltonian.

Next we will present new fourth-order numerical methods in terms of products of exponentials of linear combinations of the integrals $\int_0^\tau \mathbf{H}(t)\, dt$ and $\int_0^\tau t\, \mathbf{H}(t)\, dt$, for a time-step $\tau$. These new methods will preserve the same qualitative properties of the exact solution as the previous second order methods.

It is known that $\exp(\Omega_1 + \Omega_2)$ gives a fourth order method in the time-step $\tau$ [12], but the presence of multidimensional integrals of commutators of $\mathbf{H}(t)$ can make it difficult to apply in some problems. In order to obtain methods which can be used with different quadratures, the $\Omega_i$ of the Magnus series have been written in terms of unidimensional integrals [13], where

$$\Omega^{[4]} \equiv \Omega_1 + \Omega_2 = H^{(0)} - [H^{(0)}, H^{(1)}] + O(\tau^5) \tag{10}$$

with

$$H^{(k)} = -\frac{i}{\tau^k} \int_{t_n}^{t_n+\tau} \Big( s - (t_n + \frac{\tau}{2}) \Big)^k \, \mathbf{H}(s)\, ds. \tag{11}$$

$k = 0, 1$. If we can not solve the integrals analytically (or it is expensive), we can do it numerically. Observe that no conditions on the points where $\mathbf{H}(t)$ has to be evaluated is required. At the same time, the evaluations used for approximating $H^{(0)}$ can be reused for the calculation of $H^{(1)}$ so, we can obtain the whole method at the cost of the evaluations of only one quadrature. If $\mathbf{H}(t)$ is only known at equidistant points it is interesting to use the Simpson rule but in general the use of the Gaussian quadrature will give the most accurate scheme.

In order to avoid the presence of (usually troublesome) commutators, we will follow the technique used for splitting methods for separable Hamiltonians. Using the BCH formula and taking (10) for order conditions, we can obtain, for example, the following fourth-order approximations with two and three exponentials,

$$\mathbf{U} = e^{\Omega^{[4]}} + O(\tau^5) = e^{\frac{1}{2}H^{(0)}+2H^{(1)}}\, e^{\frac{1}{2}H^{(0)}-2H^{(1)}} + O(\tau^5) \tag{12}$$

$$= e^{H^{(1)}}\, e^{H^{(0)}}\, e^{-H^{(1)}} + O(\tau^5), \tag{13}$$

where we have used the fact that $H^{(0)} = O(\tau)$ and $H^{(1)} = O(\tau^2)$. It is straightforward to prove that the new methods are time-symmetric. That is: if we integrate the equations from 0 to $t$ and next we integrate from $t$ to 0 using the numerical method after changing the sign of the time ($t$) we will recover the same initial conditions.

A deeper analysis in order to look for more sophisticated and efficient methods for special structures of $\mathbf{H}(t)$ as well as higher order methods will be analysed in [17]. In most cases, the schemes (12) and (13) have similar accuracy.

If the Hamiltonian is separable in exactly solvable parts, as is the case of (7) then, the linear combination $\alpha H^{(0)} + \beta H^{(1)} = (\alpha T^{(0)} + \beta T^{(1)}) + (\alpha V^{(0)} + \beta V^{(1)})$ is also separable in two exactly solvable parts, where $T^{(k)}$ and $V^{(k)}$ have the same structure as $H^{(k)}$ after substituting (11) into $\mathbf{H}$ by $\mathbf{T}$ and $\mathbf{V}$, respectively. Then, each exponential can be evaluated using standard splitting methods [14, 15, 16]. It is very important to notice that if in (7) $\mathbf{T}$ is quadratic in the momenta then it is possible to use Runge-Kutta-Nyström (RKN) methods, which are, in general, considerably more efficient than standard Partitioned Runge-Kutta (PRK) methods. In [17] we will analyse the more efficient splitting methods we found in the literature in the following cases: (1) $\mathbf{T}$ and $\mathbf{V}$ have general structure; (2) $\mathbf{T}$ is quadratic in the momenta (RKN); (3) both $\mathbf{T}$ and $\mathbf{V}$ are quadratic in the momenta and coordinates, respectively (we will refer to them as RKN2).

**CLASSICAL APPROXIMATION**. In general, $\mathbf{H}(t)$ is a real symmetric time-dependent matrix and it is then possible to avoid working with complex vectors considering the following $N$-dimensional real vectors: $\mathbf{q} = \mathrm{Re}\,\mathbf{c}$ and $\mathbf{p} = \mathrm{Im}\,\mathbf{c}$. The evolution of the system is then given by

$$\frac{d}{dt}\left\{\begin{array}{c}\mathbf{q}\\ \mathbf{p}\end{array}\right\} = J\otimes\mathbf{H}(t)\left\{\begin{array}{c}\mathbf{q}\\ \mathbf{p}\end{array}\right\} \qquad \text{with} \quad J\otimes\mathbf{H}(t) \equiv \left(\begin{array}{cc} 0 & \mathbf{H}(t) \\ -\mathbf{H}(t) & 0 \end{array}\right). \tag{14}$$

This equation is usually related to the evolution of a classical Hamiltonian system with $\mathbf{q}$ and $\mathbf{p}$ being the coordinates and momenta. The corresponding Hamiltonian function is $\mathcal{H} = \frac{1}{2}\mathbf{p}^T\mathbf{H}(t)\mathbf{p} + \frac{1}{2}\mathbf{q}^T\mathbf{H}(t)\mathbf{q}$.

Our approach is to apply the methods presented in the previous section to this problem. Then, for obtaining second order methods we can define

$$\mathbf{V}_{c,k} \equiv \left(\begin{array}{cc} 0 & 0 \\ -\mathbf{H}_k & 0 \end{array}\right); \qquad \mathbf{T}_{c,k} \equiv \left(\begin{array}{cc} 0 & \mathbf{H}_k \\ 0 & 0 \end{array}\right) \tag{15}$$

with $\mathbf{H}_k = \mathbf{H}(t_n + k\tau)$, $\;k = 0, \frac{1}{2}, 1$. Then a scheme similar to (9) can be used, where $\exp(\mathbf{T}_{c,k}) = \mathbf{I} + \mathbf{T}_{c,k}$ and $\exp(\mathbf{V}_{c,k}) = \mathbf{I} + \mathbf{V}_{c,k}$. In this case it is more efficient to replace $\mathbf{T}_{1/2}$ by $\frac{1}{2}(\mathbf{T}_{c,0} + \mathbf{T}_{c,1})$ in (9), hence the method will require only one evaluation of $\mathbf{H}(t)$ per step.

In the calculation of the vector-matrix multiplications $\mathbf{Hq}$ and $\mathbf{Hp}$ we can consider real FFTs when evaluating the kinetic energy. Finally, since the last exponential can be evaluated together with the first one in the next step, the method requires one evaluation of the time-dependent matrix $\mathbf{H}(t)$ and four real FFTs per step, which is equivalent with two complex FFTs giving a cost similar to that of (9).

There are, however, some qualitative differences. Scheme (9) applied to (7) preserves unitarity because each exponential is an unitary operator. On the other hand in the classical case, the unitarity is preserved only if the vector $(\mathbf{q}, \mathbf{p})$ evolves through an orthogonal transform, which is not the case if we split the matrix in the form (15). The unitarity is not preserved exactly but, in most cases it is not seriously perturbed due to the preservation of symplecticity [3, 4, 10] (symplecticity is a necessary, but not sufficient, condition for unitarity). Scheme (9) is useful only if the Hamiltonian can be split in two exactly solvable parts, while scheme (15) can be used independently of the structure of $\mathbf{H}$. Alternatively the extrapolation technique from [18] can be utilised, giving schemes with arbitrarily accurate unitarity while still retaining symplecticity.

If we define now

$$H_c^{(k)} \equiv \frac{1}{\tau^k} J \otimes \int_{t_n}^{t_n+\tau} \left(s - (t_n + \frac{\tau}{2})\right)^k \mathbf{H}(s)\, ds \equiv \left( \begin{array}{cc} 0 & \mathbf{H}^{(k)} \\ -\mathbf{H}^{(k)} & 0 \end{array} \right), \quad (16)$$

$k = 0, 1$, we can use the fourth-order methods (12) and (13) substituting $H^{(k)}$ for $H_c^{(k)}$. In this case $H_c^{(k)}$ is always separable in two exactly solvable parts, e.g.

$$V_c^{(k)} \equiv \left( \begin{array}{cc} 0 & 0 \\ -\mathbf{H}^{(k)} & 0 \end{array} \right); \qquad T_c^{(k)} \equiv \left( \begin{array}{cc} 0 & \mathbf{H}^{(k)} \\ 0 & 0 \end{array} \right) \quad (17)$$

with $k = 0, 1$. Observing that $[T_c^{(0)}, T_c^{(1)}] = [V_c^{(0)}, V_c^{(1)}] = 0$ and

$$[T_c^{(0)}, [T_c^{(0)}, [T_c^{(0)}, V_c^{(0)}]]] = [V_c^{(0)}, [V_c^{(0)}, [V_c^{(0)}, T_c^{(0)}]]] = 0 \quad (18)$$

it can be shown that very efficient RKN2 methods can be used [3].

**NUMERICAL EXPERIMENTS**. In order to appreciate the efficacy of the methods presented in this letter we will consider the Hamiltonian of a diatomic molecule with a linear time-dependent perturbation

$$\hat{H} = -\frac{1}{2\mu} \frac{\partial^2}{\partial x^2} + V(x) + x f(t), \quad (19)$$

where $\mu$ is the reduced mass of the diatomic molecule. We will consider the Morse potential, $V(x) = D\,(1 - e^{-\alpha x})^2$, as a good approximation for the study of the vibrational states of a diatomic molecule [19]. $D$ being the dissociation energy and $\alpha$ the length parameter. The unperturbed system has 24 bounded states with energies $E_n = \left(n + \frac{1}{2}\right) \omega_0 - \left(n + \frac{1}{2}\right)^2 \frac{\omega_0^2}{4D}$, $n = 0 \ldots 23$, where $\omega_0 = \alpha\sqrt{2D/\mu}$. In particular we will study the HF molecule, whose parameters are: $\mu = 1745\ a.u.$, $D = 0.2251\ a.u.$ and $\alpha = 1.1741\ a.u.$ For the time-dependent perturbation we will consider the following two cases:

1) Interaction with a laser field: $f(t) = A\cos(\omega t)$. We will consider three cases: *a*) $A = 0.0011025\, a.u.$ and $\omega = 0.193\, \omega_0$ (the Rabi frequency)

according to [19], $b)$ $A = 0.011025\,a.u.$ and $\omega = 0.9476\,\omega_0$ as in [10], and $c)$ $\omega = 5\omega_0$ with $A = 0.011025\,a.u.$

2) Collision with an atom: $f(t) = \frac{A\omega}{\cosh^2(B\sqrt{\omega}t)}$, where $\omega$ is proportional to the energy of the collision and $A, B$ are parameters of the system. We will use $A = 0.385\,a.u.$, $B = 2.5\,a.u.$ which are consistent with the model of [20], and we will take $\omega = 50\omega_0$.

As initial condition we take the ground state of the Morse oscillator, $\psi_0(x) = R\exp(-\beta x)\exp\left(-\gamma e^{-\alpha x}\right)$, with $\gamma = 2D/\omega_0$, $\beta = (\gamma - 1/2)\alpha$ where $R$ is the normalisation constant. The grid for the spatial coordinate $x$ ranges from $-0.8$ to $4.32$ with $N = 64$ with periodic boundary conditions assumed. To gauge accuracy, we consider the instantaneous mean energy of the diatomic molecule $E(t) = \langle \mathbf{c}(t)|\frac{1}{2}\mathbf{P}^2 + \mathbf{V}(\mathbf{X})|\mathbf{c}(t)\rangle$.

From (16) we have that

$$\mathbf{H}^{(0)} = \frac{h}{2}\mathbf{P}^2 + h\mathbf{V}(\mathbf{X}) + \mathbf{X}f^{(0)}; \qquad \mathbf{H}^{(1)} = \mathbf{X}f^{(1)} \tag{20}$$

where $\mathbf{V}(\mathbf{X})$ and $\mathbf{X}$ are $N \times N$ diagonal matrices with $V(x_k)$ and $x_k$ in the diagonal respectively. $\mathbf{P}^2$ is the matrix associated with the kinetic energy and $f^{(i)} = \frac{1}{\tau^i}\int_{t_n}^{t_n+\tau}\left(s - (t_n + \tau/2)\right)^i f(s)\,ds, \quad i = 0, 1$. Observe that now the matrices are time-independent and the problem will be to evaluate the exponentials when using the methods (12) and (13). As mentioned previously, there myriads of methods available for evaluating the exponential of a matrix and the proper choice dependes on the particular Hamiltonian. Observe that the exponentials of (17) are very cheap to evaluate through

$$e^{V_c^{(k)}}\left\{\begin{array}{c}\mathbf{q}\\ \mathbf{p}\end{array}\right\} = \left\{\begin{array}{c}\mathbf{q}\\ \mathbf{p} - \mathbf{H}^{(k)}\mathbf{q}\end{array}\right\}; \qquad e^{T_c^{(k)}}\left\{\begin{array}{c}\mathbf{q}\\ \mathbf{p}\end{array}\right\} = \left\{\begin{array}{c}\mathbf{q} + \mathbf{H}^{(k)}\mathbf{p}\\ \mathbf{p}\end{array}\right\} \tag{21}$$

requiring only one real FFT/inverse FFT for evaluating the kinetic part in $\mathbf{H}^{(k)}\mathbf{q}$ and $\mathbf{H}^{(k)}\mathbf{p}$. Then, we can use splitting methods in the form

$$e^{\tau(A+B)} = \prod_{i=1}^{m} e^{a_i\tau A}\, e^{b_i\tau B} + O(\tau^k), \tag{22}$$

with $k > 4$. Then, for the exponentials in (12) we can consider that $\frac{1}{2}H_c^{(0)} \pm 2H_c^{(1)} = A + B$ with $A = \frac{1}{2}V_c^{(0)} \pm 2V_c^{(1)}$ and $B = \frac{1}{2}T_c^{(0)} \pm 2T_c^{(1)}$, where $\frac{1}{2}\mathbf{H}^{(0)} \pm 2\mathbf{H}^{(1)} = \frac{h}{4}\mathbf{P}^2 + \frac{h}{2}\mathbf{V}(\mathbf{X}) + \mathbf{X}\left(\frac{1}{2}f^{(0)} \pm 2f^{(1)}\right)$. Property (18) allows us to use RKN2 methods, and in [3] we can find solutions for $\{a_i, b_i\}_{i=1}^m$ for several values of $m$ and $k$ up to $k = 12$. These families of methods are very accurate, have good stability properties and preserve unitarity up to order $k+1$. If we use one of these methods for $\exp(\frac{1}{2}H_c^{(0)} + 2H_c^{(1)})$ and its adjoint for $\exp(\frac{1}{2}H_c^{(0)} - 2H_c^{(1)})$ then, the total number of stages is reduced by one, leaving the total composition symmetric and in addition the unitarity is preserved up to order $k+2$. In our examples we will consider the methods of [3] with $m = k = 4$ and $m = k = 6$.

In case of scheme (13), $\exp(H_c^{(0)})$ can be evaluated in a similar fashion and $\exp(H_c^{(1)})$ is exactly and easily computed because $\mathbf{H}^{(1)}$ is a diagonal matrix. Thus the overall cost per step will be less than for scheme (12). In the following we denote schemes (12) and (13) by 2EX-$k$ and 3EX-$k$ respectively, with $k = 4, 6$ depending which splitting method of [3] is applied to compute the exponential.

For comparison we consider the approach presented in [10] for problem (14) with associated Hamiltonian $\mathcal{H} = \frac{1}{2}\mathbf{p}^T\mathbf{H}(t)\mathbf{p} + \frac{1}{2}\mathbf{q}^T\mathbf{H}(t)\mathbf{q}$. This Hamiltonian can be rewritten in the form $\widetilde{\mathcal{H}} = \left(\frac{1}{2}\mathbf{p}^T\mathbf{H}(p_{2t})\mathbf{p} + p_{1t}\right) + \left(\frac{1}{2}\mathbf{q}^T\mathbf{H}(q_{1t})\mathbf{q} - q_{2t}\right)$, where the new coordinates $q_{1t}$ and $q_{2t}$ and their associated momenta $p_{1t}$ and $p_{2t}$ are introduced in order to obtain a time independent Hamiltonian, which is separable in two exactly solvable parts. Observe that $\mathcal{H}$ is quadratic in the coordinates and momenta, but this is not necessarily the case of $\widetilde{\mathcal{H}}$. Then, the number of allowed methods is considerable reduced, i.e. it is not possible to use RKN2 methods. We will consider the five stage fourth order $(S, m = 5)$ and the nine stage sixth order $(SS, m = 9)$ methods given in [16], which are the most efficient fourth and sixth order symmetric PRK method we found. The methods will be referred to as McL-4 and McL-6.

In figure 1a we consider the laser field perturbation through 100 periods of the laser frequency ($T = 100\frac{2\pi}{\omega}$) and display the average relative error in energy (the average is taken over 5-10 consecutive solution points). The time-step used is very similar for all three examples and is chosen such that all methods require 16000, 4000 and 640 FFTs per period respectively.

There are two sources of error in our methods: the truncated Magnus approximation for the time-dependent part and the splitting approximation of the exponential. It seems clear that for smooth time-dependent functions the error of Magnus is very small and the main error comes from the splitting method. Thus in this case one should to use the most accurate and stable splitting methods (2EX-6). In figure 1b the system is simulated near the resonant frequency and the contribution to the total error comes equally from the splitting method and the Magnus approximation, so in this case best choice is to use the cheapest Magnus scheme together with a good splitting method i.e. (3EX-6). Finally, for highly oscillating(in 't') functions the largest errors will originate from the Magnus expansion and thus the cheapest

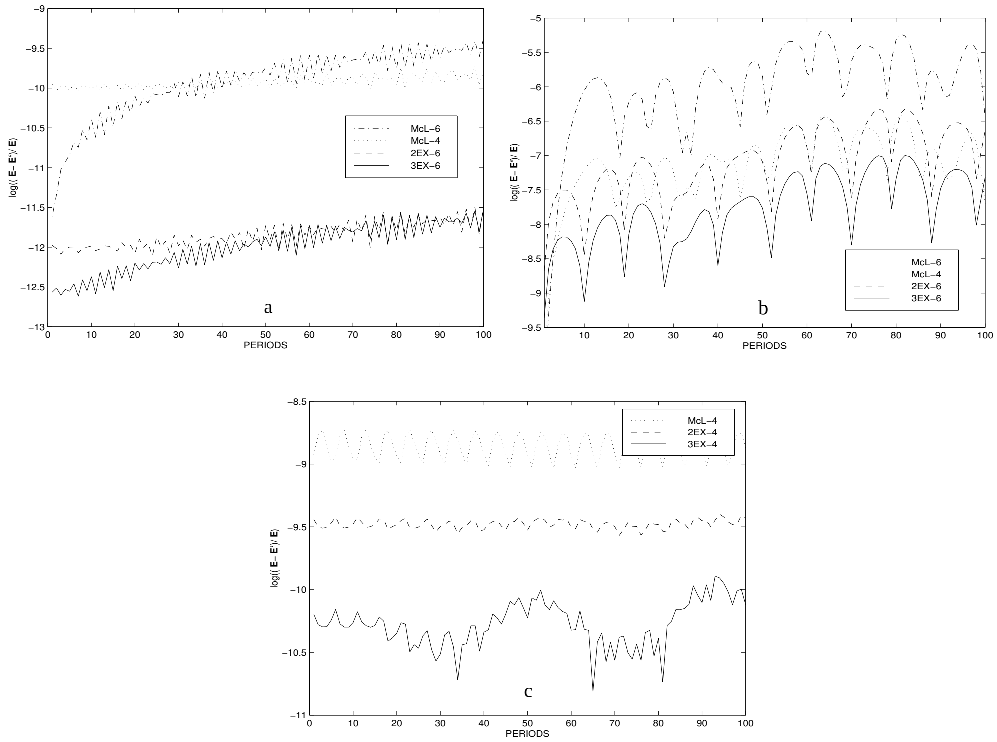


Figure 1: Average relative errors in energy through 100 periods for the laser field perturbation for: a) $A = 0.0011025$, $\omega = 0.193\omega_0$ with 16000 FFT/period b) $A = 0.011025$, $\omega = 0.9476\omega_0$ with 4000 FFT/period and c) $A = 0.011025$, $\omega = 5\omega_0$ with 640 FFTs/period. (McL-6 is in this case unstable.)

splitting method (3EX-4) will be the optimal choice (figure 1c).

The Magnus approximation integrates the time dependent part more accurately than the standard splitting methods with the number of time-dependent function evaluations considerably reduced. Furthermore the accuracy improves with increase in frequency.

In Table 1 we present, for the near resonant case (as in figure 2), the stability limit (time-step and number of FFTs), the average error in the preservation of unitarity ($|\langle \mathbf{c}(t)|\mathbf{c}(t)\rangle - 1|$) and the number of time-dependent evaluations per period required for each method. The new methods have better stability limit, allowing bigger time-steps, also they preserve unitarity more accurately. In addition, if the evaluation of the time-dependent part of the potential is expensive the efficacy is even more clear.

In figure 2 we present the error in energy versus the number of FFT for the collision problem. The integration was carried out for $t \in [-\frac{10}{B\sqrt{\omega}}, \frac{10}{B\sqrt{\omega}}]$

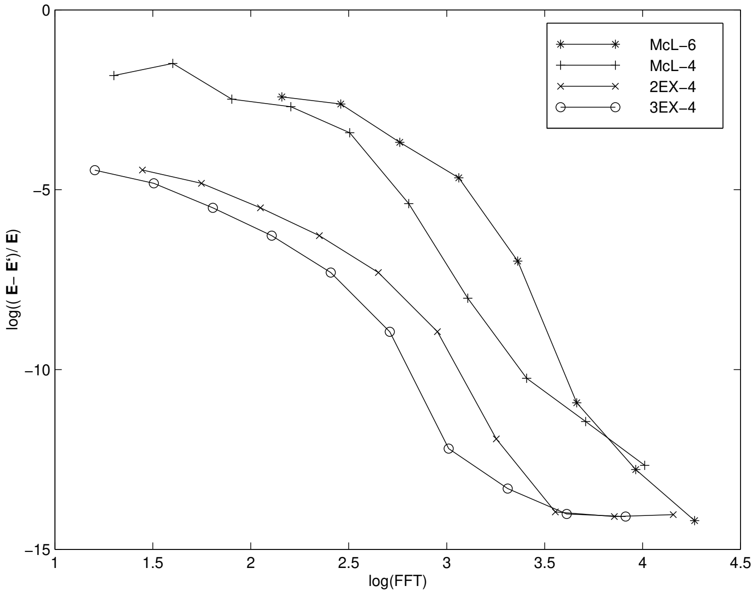


Figure 2: Average relative errors in energy vs number of FFTs for the collision problem, with step-sizes starting at the stability limit and from there on decreasing. Methods 2EX-4 and 3EX-4 quickly reach the machine accuracy before displaying the expected 4th order accuracy.

with $\omega = 50\,\omega_0$, starting at the stability limit and from there on decreasing the time-steps. As mentioned, the superiority of the new methods is clearer if the time-dependent functions oscillates quickly. Similar experiments for other values of $\omega$ were carried confirming this fact.

In conclusion we can say that the methods presented provide a superior alternative to the approach presented in [10]. The approach lends itself to high accuracy computations of Schrödinger equations with time-dependent potentials. The methods retain symplecticity exactly while unitarity is conserved to high order($> 4$). In [17] we present how the approach presented in this letter for linear equations, easily can be adapted to non-linear, time-dependent classical Hamiltonian systems, retaining symplecticity and time-symmetry for high accuracy, long term computation of such systems.

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| | Stability | | Error in | Function |
|---|---|---|---|---|
| | $\tau$ | FFT | unitarity | evaluations |
| 2EX-4 | 14.0 | 700 | 6.8e-13 | 285 |
| 2EX-6 | 11.3 | 1364 | 1.2e-14 | 182 |
| 3EX-4 | 5.5 | 1024 | 9.7e-12 | 500 |
| 3EX-6 | 6.9 | 1224 | 1.1e-13 | 333 |
| McL-4 | 4.7 | 1500 | 8.5e-9 | 2000 |
| McL-6 | 4.0 | 3168 | 1.8e-9 | 2000 |

Table 1: Further results showing stability limits, unitarity and function evaluations for experiment 1b. The columns $\tau$ and FFT shows the stability limit in terms of longest time-step(in a.u.), while FFT shows the corresponding number of fast fourier transforms. The error in unitarity is an average error over all time-steps. The number of function evaluations is the number of times the potential is evaluated per period.

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