Numerical Solution of the Time-Dependent Schrödinger Equation in Ultrafast Laser Dynamics*

OTHMAR KOCH

Institute for Analysis and Scientific Computing
Vienna University of Technology
Wiedner Hauptstrasse 8–10, A-1040 Wien
AUSTRIA

Abstract: The numerical approximation of the solution of the time-dependent Schrödinger equation arising in ultrafast laser dynamics is discussed. The linear Schrödinger equation is reduced to a computationally tractable, lower dimensional system of nonlinear partial differential equations by the *multi-configuration time-dependent Hartree-Fock method*. This method serves to approximate the original wave function on a nonlinear manifold, using the antisymmetry inherent in the model to significantly reduce the dimension of the solution space. For the solution of the resulting systems of PDEs, several numerical techniques are compared. Space discretization using the pseudospectral method turns out to be superior to finite difference approximations. For time integration, the range of applicability and computational efficiency of high-order Runge-Kutta methods are compared with *variational splitting*, a method recently proposed for quantum molecular dynamics.

Key-Words: Time-dependent Schrödinger equation, multi-configuration time-dependent Hartree-Fock method, variational splitting, pseudospectral method.

1 Introduction

This paper discusses the numerical properties of a new approach to the numerical solution of the time-dependent Schrödinger equation arising in ultrafast laser dynamics.

Large-scale computations of electronic structure and dynamics pose extremely challenging problems in several areas of research. For static electronic structure computations, many different methods have been developed in various fields, such as theoretical physics or theoretical and computational chemistry. To improve on the solution of the time-independent Schrödinger equation by direct discretization, methods like *density functional theory (DFT)* or *(multi-configuration) Hartree-Fock (MCHF)* have been suggested.

Ultrashort strong laser pulses, however, require the solution of time-dependent initial value problems. These laser pulses developed during the last few years have opened a new regime in the interaction of fields with matter [7]. One of the most intriguing aspects is the possibility of ultrashort time-resolved spectroscopy in the sub-femtosecond time domain.

The present state of the art of numerically solving the time-dependent Schrödinger equation directly for realistic laser pulses is limited to two electron systems. The most successful calculations involve the largest massively parallel computers available [1], [9]. It is clear that the direct solution of the linear time-dependent Schrödinger equation has reached its computational limits.

The use of time-dependent density functional theory for this problem is limited at least by two problems: The known approximations of the crucial "exchange correlation" term, while producing consistent ground state energies, generate contradictory and incorrect dynamical behavior [11] and there is no applicable theory for the description of multi-electron processes, such as detachment of two electrons from an atom. While this approach promises an enormous reduction in the complexity of the computational problems, the theory is not yet developed far enough so as to be applicable to our problem, see also [13].

Therefore the present state of the art to make the original, linear Schrödinger equation tractable for numerical computation is the multi-configuration time-dependent Hartree-Fock method (MCTDHF) proposed in [3], [12], [13]. This approach produces a lower-dimensional, nonlinear system of coupled Schrödinger equations. The method excels in its favorable scaling of the computational complexity in re-

---

lation to the number of particles in the model, thus making a simulation of systems with up to ten particles feasible, see [12].

2 The MCTDHF Method

The model to be solved is the time-dependent Schrödinger equation for an atom or molecule with f degrees of freedom in a time-dependent electric field (typically arising from ultrashort laser pulses),

$$\mathrm{i}\frac{\partial \psi}{\partial t} = H\psi, \tag{1}$$

where the *wave function* $\psi = \psi(x_1, \ldots, x_f, t)$ explicitly depends on time t and, in the case considered here, the positions $x_1, \ldots, x_f$ of electrons in an atom or molecule. The Hamiltonian H is time-dependent and has the form

$$
\begin{aligned}
H \quad := \quad & \sum_{k=1}^{f} \left(\frac{1}{2} \left(-\mathrm{i}\nabla_k - A(t) \right)^2 + \cdots \right. \\
& \left. + U(x_k) + \sum_{l \neq k} V(x_k - x_l) \right),
\end{aligned} \tag{2}
$$

where

$$U(x) := -\sum_{l=1}^{f} \frac{1}{\sqrt{a^2 + (x - 1.4l)^2}}, \tag{3}$$

$$V(x - y) := \frac{1}{\sqrt{1 + (x - y)^2}}, \tag{4}$$

$$A(t) := \mathrm{e}^{-(t/\tau)^2} \sin(\omega t) A_0. \tag{5}$$

∇_k is the nabla operator w. r. t. x_k only. For this potential, the internuclear distance is fixed at 1.4, and for each molecule the screening parameter a is adjusted such that the ionization potential is 0.3 independent of f [12], [13]. In the case $f = 2$ which we focus on in this paper, $a = 1.28$ holds. Moreover, ω is of order of magnitude 10^{-1}, $\tau = \frac{2\pi}{\omega}n$, where $n \in \mathbb{R}$ is of order of magnitude 10, and A_0 is a constant, $A_0 = O(1)$. For the moment, only problems in one space dimension are considered.

In [3], [12], [13], a new approach for the approximate solution of the time-dependent Schrödinger equation is introduced: The multi-electron wave function ψ from (1) is approximated by a function satisfying the ansatz

$$
\begin{aligned}
\psi \quad = \quad & \sum_{(j_1, \ldots, j_f)} a_{j_1, \ldots, j_f}(t) \phi_{j_1}(x_1, t) \cdots \phi_{j_f}(x_f, t) \\
=: \quad & \sum_J a_J \Phi_J(x, t).
\end{aligned} \tag{6}
$$

In (6), only solutions ψ are considered which are antisymmetric under exchange of any two of their arguments x_j, x_k. This assumption is particular to the MCTDHF approach, as compared to the multi-configuration time-dependent Hartree method (MCTDH) considered, for example, in [2] or [8] for quantum molecular dynamics, and reduces the number of equations considerably. Particularly, the assumption implies antisymmetry in the coefficients a_J. Formally, multi-indices $J = (j_1, \ldots, j_f)$ vary for $j_k = 1, \ldots, N$, $k = 1, \ldots, f$. Due to the simplifications resulting from the symmetry assumption, only $\binom{N}{f}$ equations for a_J have to be solved in the actual computations, however.

The *Frenkel-Dirac variational principle* is used to derive differential equations for the coefficients a_J and the *single-particle functions* ϕ_k. Thus, it is required that for ψ in the manifold $\mathcal{M}$ of functions of the form of the ansatz (6),

$$\left\langle \delta\psi \left| \mathrm{i}\frac{\partial}{\partial t} - H \right| \psi \right\rangle = 0 \tag{7}$$

holds, where $\delta\psi$ varies in the tangent space $\mathcal{T}_\psi\mathcal{M}$ of $\mathcal{M}$ at ψ.

In order to define a unique solution of (7), the additional constraints

$$\langle \phi_j | \phi_k \rangle = \delta_{j,k}, \quad t = 0, \tag{8}$$

$$\left\langle \phi_j \left| \frac{\partial \phi_k}{\partial t} \right. \right\rangle = -\mathrm{i}\left\langle \phi_j \left| g \right| \phi_k \right\rangle, \quad t \geq 0, \tag{9}$$

are imposed, where any Hermitian operator g may be used. Often, $g \equiv 0$ is chosen for reasons of simplicity, but for our numerical treatment nontrivial g cannot be neglected [6]. (8) together with (9) guarantees that the relation from (8) holds for all $t \geq 0$, see [6].

The variational principle (7) and the additional restrictions (8) and (9) finally yield the *working equations*

$$\mathrm{i}\frac{da}{dt} = A_H(\phi)a, \tag{10}$$

$$\mathrm{i}\frac{\partial \phi}{\partial t} = B_H(a, \phi)\phi, \tag{11}$$

for $a = (a_{j_1, \ldots, j_f})$, $\phi = (\phi_k)$. In equation (10),

$$[A_H(\phi)]_{J,L} := \langle \Phi_J | H | \Phi_L \rangle \tag{12}$$

is a *Galerkin matrix*, and (11) is derived from

$$\mathrm{i}\rho\frac{\partial \phi}{\partial t} = (I - P)\overline{H}\phi, \tag{13}$$

where

$$\psi_j := \langle \phi_j | \psi \rangle, \qquad (14)$$

$$\rho_{j,l} := \langle \psi_j | \psi_l \rangle, \qquad (15)$$

$$\overline{H}_{j,l} := \langle \psi_j | H | \psi_l \rangle, \qquad (16)$$

and P is the orthogonal projector onto the space spanned by the functions ϕ_k. In (14), the L^2 scalar product defining the *single hole functions* is defined with respect to the argument of ϕ_j only, while for the *density matrix* in (15) the integration is defined over all variables except one, and the *mean-field operator matrix* from (16) contains operators acting on one spatial variable, say x_k.

Using numerical approximations for the scalar products in the definitions of A_H and B_H in (10) and (11), these working equations constitute the mathematical model that is to be solved.

3 Numerical Methods

To compute the solution of (10) and (11) numerically, the method of lines is used. First, space discretization is applied to derive a system of ordinary differential equations. To this end, two different schemes are employed. Originally, second order finite differences on an equidistant mesh with mesh width Δx were used to discretize the first and second derivatives in the space variable occurring in the Hamiltonian from (2) [12], i.e.,

$$\phi_j'(x,t) \approx \frac{\phi_j(x+\Delta x,t) - \phi_j(x-\Delta x,t)}{2\Delta x},$$

$$\phi_j''(x,t) \approx \frac{\phi_j(x+\Delta x,t) - 2\phi_j(x,t) + \phi_j(x-\Delta x,t)}{(\Delta x)^2}$$

for the single-particle functions ϕ_j. This naive approximation has certain disadvantages. The approximation of the continuous Hamiltonian operator H is not valid for the whole spectrum of this operator [3]: The approximation quality is $O((\Delta x)^2)$ in general, see Section 4, only small eigenvalues are approximated well. Consequently, the pseudospectral method is used as a standard for space discretization. The application of the kinetic part of the Hamiltonian H (which contains the derivatives w.r.t. the spatial variable) to a single-particle function $\phi_j(x,t)$ is thus approximated by

$$(-\mathrm{i}\nabla - A(t))^2 \approx DFT^{-1} \circ (-\mathrm{i}D - A(t))^2 \circ DFT,$$

where

$$D := \mathrm{diag}\left(\frac{k\pi}{x_{\mathrm{end}}}\right), \quad k = -K, \dots, K-1.$$

The vector of Fourier coefficients (which depend on time t) on an equidistant spatial grid $(x_{-K}, \dots, x_K)$ defined on the interval $[-x_{\mathrm{end}}, x_{\mathrm{end}}]$ by the *discrete Fourier transform DFT* is given by $\hat{U}(t) = (\hat{u}_{-K}(t), \dots, \hat{u}_{K-1}(t)) = DFT(\phi_j)$, and conversely $(\phi_j(x_{-K}, t), \dots, \phi_j(x_{K-1}, t)) = DFT^{-1}(\hat{U})$, with

$$\hat{u}_k(t) := \frac{1}{2K} \sum_{l=-K}^{K-1} \exp\left(-\frac{\mathrm{i}k\pi x_l}{x_{\mathrm{end}}}\right) \phi_j(x_l, t),$$

$$\phi_j(x_l, t) := \sum_{k=-K}^{K-1} \exp\left(\frac{\mathrm{i}k\pi x_l}{x_{\mathrm{end}}}\right) \hat{u}_k(t).$$

DFT and DFT^{-1} can be efficiently computed using Fast Fourier Transforms (FFT) [10].

For time integration, two methods are considered here. Most simply, the working equations (10) and (11) are solved by the classical, explicit Runge-Kutta method of order four, after applying either of the space discretization schemes described above. Alternatively, *variational splitting* is used, which was proposed in [8] for the solution of the nonlinear PDEs arising from MCTDH. In this method, the Hamiltonian $H := T + V$ from (2) is split into the parts

$$T := \sum_{k=1}^{f} \left(\frac{1}{2} (-\mathrm{i}\nabla_k - A(t))^2 + U(x_k) \right), \quad (17)$$

$$V := \sum_{k=1}^{f} \sum_{l \neq k} V(x_k - x_l). \qquad (18)$$

One step of the variational splitting method starting at $t = t_0$ with time step Δt is defined as follows:

1. Compute $\psi_{1/2}^{-} \in \mathcal{M}$ as the solution at time $t_0 + \frac{1}{2}\Delta t$ of

$$\left\langle \delta\psi \left| \mathrm{i}\frac{\partial}{\partial t} - T \right| \psi \right\rangle = 0 \quad \forall \delta\psi \in \mathcal{T}_\psi \mathcal{M}, \quad (19)$$

with initial value $\psi(t_0) = \psi_0$ ("T step").

2. Compute $\psi_{1/2}^{+} \in \mathcal{M}$ as the solution at time $t_0 + \Delta t$ of

$$\left\langle \delta\psi \left| \mathrm{i}\frac{\partial}{\partial t} - V \right| \psi \right\rangle = 0 \quad \forall \delta\psi \in \mathcal{T}_\psi \mathcal{M}, \quad (20)$$

with initial value $\psi(t_0) = \psi_{1/2}^{-}$ ("V step").

3. Compute $\psi_1 \in \mathcal{M}$ as the solution at time $t_0 + \Delta t$ of (19) with initial value $\psi(t_0 + 1/2\Delta t) = \psi_{1/2}^{+}$.

This symmetric splitting yields a second order approximation for the solution of the full problem (7) [8].

Now, since $T\psi \in \mathcal{T}_\psi \mathcal{M}$ for $\psi \in \mathcal{M} \cap H^2$, the two steps of the form (19) are equivalent to solving the Schrödinger equations

$$\mathrm{i}\frac{\partial\psi}{\partial t} = T\psi \tag{21}$$

on the respective domains. If the initial function is chosen in $\mathcal{M}$, (21) decouples into a set of single particle Schrödinger equations:

$$\frac{da_J}{dt} = 0, \quad \forall J, \tag{22}$$

$$\mathrm{i}\frac{\partial\phi_j}{\partial t} = \frac{1}{2}\left(-\mathrm{i}\nabla - A(t)\right)^2 \phi_j + U\phi_j, \quad \forall j. \tag{23}$$

The second splitting step (20) leads to equations

$$\mathrm{i}\frac{da}{dt} = A_V(\phi)a, \tag{24}$$

$$\mathrm{i}\frac{\partial\phi}{\partial t} = B_V(a,\phi)\phi, \tag{25}$$

where A_V and B_V are defined analogously as in (10) and (11), using the operator V instead of H.

The single particle Schrödinger equations (22) and (23) are alternatively solved by the box scheme (where the special form of the resulting system of linear equations is exploited [6]) or, more efficiently, by the pseudospectral method in conjunction with the exponential midpoint rule [4], [6], see Section 4.

For the solution of the *reduced working equations* (24) and (25), various (second-order) schemes can be employed. It turned out that the choice of the numerical integrator for these equations is not critical, since the reduced working equations do not suffer from the unsmoothness of the space discretization of the (unbounded) differential operator T. Two (implicit) schemes proposed in [8] and an explicit second order Runge-Kutta method were implemented and found to perform equally well, see also [5], [6].

4 Numerical Results

In this section the numerical properties of the solution methods described above are demonstrated and the performance of the methods is compared. The *electron density*

$$\langle\psi|\psi\rangle$$

serves as a convenient observable, where the scalar product above is defined w. r. t. all but one spatial variable. The spatial grid is defined for $x_{\mathrm{end}} = 100$,

where usually $K = 500$ is chosen, and time integration is performed on the interval $[-110, 110]$. For the assessment of the numerical methods, the numerical approximations are compared at 13 points in the time grid spaced equidistantly in $[0, 110]$, where the maximal error is taken at all spatial grid points, respectively. For absolute errors, the maximum norm over the points in the time grid is used, while relative errors are computed at $t = 110$ only, because the absolute values of the electron density remote from the origin are too small to admit a meaningful definition of the relative error in the first few steps of time integration, see [5]. We focus on the case where $N = f = 2$ which reflects the properties of more general configurations well, see [5]. The working equations for this case are explicitly set up in [6].

The numerical computations were performed with the MCTDHF code [3] on a Compac SC45, where the code was compiled with the Compaq Fortran 90 Compiler V5.5-1877-48BBF in IEEE double precision arithmetic.

Table 1 gives the empirical convergence orders p for the solution of (10) and (11) by the classical, explicit Runge-Kutta method of order four and for variational splitting, where finite differences are used for space discretization. p is calculated from the differences in the solutions for three different step sizes Δt in the time integration. Here, 'err' denotes the difference between two successive numerical approximations. The classical convergence orders four and two, respectively, are indeed retained throughout our tests, see also [5]. Since the error is monotonously decreasing, the solution computed by the Runge-Kutta method for $\Delta t = 6.25 \cdot 10^{-4}$ is accepted as the most accurate approximation available and used as a reference solution for the comparisons of the errors later in this section.

The main advantage of variational splitting is that the single particle Schrödinger equations and the reduced working equations can be treated independently. For (22) and (23), the discretization of the Laplacian by finite differences introduces an undesirable unsmoothness of the resulting ODEs. Consequently, the step size Δt has to be chosen very small. On the other hand, (24), (25) are smoother and allow larger step sizes. It is crucial to exploit this feature, as the evaluation of the right-hand side of (25) is the computationally most expensive part of the solution algorithm. While this is not obvious for $N = f = 2$, for larger systems the computation of B_V consumes the largest part of the overall run time of the program,

Δt	err RK	p RK	err varsplit	p varsplit
2.00E-02	—	—	—	—
1.00E-02	2.0754E-06	—	3.1665E-06	—
5.00E-03	1.6152E-06	0.36	7.6934E-07	2.04
2.50E-03	1.6775E-07	3.27	1.9085E-07	2.01
1.25E-03	1.1625E-08	3.85	4.7605E-08	2.00
6.25E-04	7.4528E-10	3.96	1.1893E-08	2.00

Table 1: Convergence for Runge-Kutta method and variational splitting, space discretization by finite differences.

T step	err	p
1	1.6357E-07	—
1/2	4.0933E-08	2.00
1/4	9.4585E-09	2.11
1/8	4.1395E-09	1.19
1/16	3.9600E-09	0.06

Table 2: Convergence for T step, variational splitting, space discretization by finite differences.

see [3], [5]. In Table 2, the errors w. r. t. the reference solution of the numerical approximations computed by variational splitting for $\Delta t = 6.25 \cdot 10^{-4}$ are given, where the step sizes used for (22) and (23) are $\Delta t/2^i$, $i = 0, \ldots, 4$, and an explicit second order Runge-Kutta method (*Heun's method*) is used to solve (24) and (25). Note that the integration methods proposed in [8] show a similar behavior [5]. The decrease of the step size for (22) and (23) reduces the error with order two for fixed Δt until the T step is solved with the same accuracy as the V step. A factor of 1/16 appears to be the optimal ratio between the two step sizes, as there is hardly any improvement in the accuracy when the step size is reduced further. With this choice of step sizes, the overall convergence order two of the method is still retained, see Table 1.

In Tables 3 and 4, the performance of the two methods is compared. Absolute and relative errors are computed w. r. t. the reference solution. In the tables, computation times (in minutes) and, more importantly, the number fcount of evaluations of B_V from (25) during the solution process is given. Note that, while the computation time for variational splitting to reach a certain level of accuracy is larger than for the Runge-Kutta method, the number fcount is comparable or even smaller for variational splitting. This implies that for larger N and f, variational splitting can be expected to perform well as compared to Runge-Kutta methods when finite differences are used for space dis-

cretization. Moreover, if the space discretization uses smaller Δx, Runge-Kutta methods become unstable while variational splitting is designed especially for this type of unsmoothness, see [5].

The results can be remarkably improved when the pseudospectral method is used for space discretization instead of finite differences. In addition to advantageous spectral properties of this approximation of the derivative of the solution [3], the error of the approximation decreases exponentially when the spatial grid is refined [10], while the error in the case of finite differences is $O((\Delta x)^2)$. To demonstrate this, the differences between the numerical solutions based on either discretization of the spatial derivative on grids with $K = 125$, $K = 250$, $K = 500$ and $K = 1000$ are considered, where the step size for time integration is chosen as $\Delta t = 6.25 \cdot 10^{-4}$ and the Runge-Kutta method is used. Thus a possible influence of the error introduced by time integration is eliminated. Table 5 gives the results. Indeed, it can be observed that the difference between the solutions computed using pseudospectral methods and finite differences, respectively, is $O((\Delta x)^2)$, whence it can be inferred that the pseudospectral method yields solutions with higher accuracy.

The ODEs resulting from space discretization by the pseudospectral method are apparently smoother than for finite differences. There is no advantage in choosing the step size for the T step smaller than for the

Δt	abs. err	rel. err	time	fcount
2.00E-02	2.7781E-06	2.1192E-03	2	44032
1.00E-02	1.7538E-06	1.8030E-03	4	88024
5.00E-03	1.7875E-07	8.0391E-04	8	176048
2.50E-03	1.2370E-08	5.2463E-05	15	352064
1.25E-03	7.4528E-10	3.0853E-06	31	704072

Table 3: Performance of Runge-Kutta method, space discretization by finite differences.

V step. Moreover, the Runge-Kutta method performs very well in this case. To demonstrate this, the errors (again calculated w. r. t. a reference solution computed by the Runge-Kutta method with $\Delta t = 6.25 \cdot 10^{-4}$), run times and number of evaluations of the right-hand side of the differential equations are given in Tables 6 and 7. Note that in this case also, both time integration schemes show their classical convergence orders four and two, respectively, see [5]. It may be concluded that for the equations resulting from the pseudospectral method, Runge-Kutta schemes yield more favorable results.

5 Conclusions

Numerical approximation methods for the solution of the time-dependent Schrödinger equation arising in ultrafast laser dynamics have been presented. It was demonstrated that pseudospectral methods are superior to finite difference approximations for space discretization of the nonlinear PDEs associated with the multi-configuration time-dependent Hartree-Fock method. Moreover, the potential of variational splitting methods for efficient time integration was assessed and the range of applicability and performance of the method was compared with explicit Runge-Kutta methods. All the numerical methods tested work satisfactorily, and the alternative methods investigated show a potential to improve the performance of standard methods. However, the best choice from among the methods tested for the numerical solution of the differential equations arising from MCTDHF is space discretization by the pseudospectral method in conjunction with time integration by explicit Runge-Kutta methods. Thus, a variable order, variable step size code based on these components is used to solve real-world problems successfully [3], [12], [13].

Acknowledgement

Δt	abs. err	rel. err	time	fcount
2.00E-02	4.1901E-06	3.0123E-03	3	22016
1.00E-02	1.0236E-06	7.5055E-04	6	44012
5.00E-03	2.5431E-07	1.8516E-04	12	88024
2.50E-03	6.3458E-08	4.5964E-05	24	176032
1.25E-03	1.5853E-08	1.1326E-05	50	352036
6.25E-04	3.9600E-09	2.6769E-06	98	704040

Table 4: Performance of variational splitting, space discretization by finite differences.

K	err	p
125	1.9052e-02	—
250	4.3354e-03	2.13
500	1.1168e-03	1.95
1000	2.7622e-04	2.01

Table 5: Convergence w. r. t. spatial grid, Runge-Kutta method.

References

[1] A. Bandrauk, A. Chelkowski, On Laser Coulomb Explosion Imaging of Proton Motion, *Chem. Phys. Letters*, Vol. 336, 2001, pp. 518–522.

[2] M. H. Beck, A. Jäckle, G. A. Worth, and H. D. Meyer, The Multiconfiguration Time-Dependent Hartree (MCTDH) Method: A Highly Efficient Algorithm for Propagating Wavepackets, *Phys. Rep.*, Vol. 324, 2000, pp. 1–105.

[3] J. Caillat, J. Zanghellini, M. Kitzler, W. Kreuzer, O. Koch, and A. Scrinzi, Correlated Multielectron Systems in Strong Laser Pulses – An MCTDHF Approach, submitted to Phys. Rev. A.

[4] T. Jahnke, C. Lubich, Error Bounds for Exponential Operator Splittings, *BIT*, Vol. 40, 2000, pp. 735–744.

[5] O. Koch, W. Kreuzer, Performance of MCTDHF Implementations, AURORA Technical Report TR-2004-14, Inst. for Anal. and Sci. Comput., Vienna Univ. of Technology, Austria, 2004.

[6] O. Koch, W. Kreuzer, and A. Scrinzi, MCTDHF in Ultrafast Laser Dynamics, AURORA TR-2003-29, Inst. for Appl. Math. and Numer. Anal., Vienna Univ. of Technology, Austria, 2003.

[7] F. Krausz, T. Brabec, Intense Few-Cycle Laser Fields: Frontiers of Nonlinear Optics, *Rev. Mod. Phys.*, Vol. 72, 2000, pp. 545–562.

[8] C. Lubich, A Variational Splitting Integrator for Quantum Molecular Dynamics, *Appl. Num. Math.*, Vol. 48, 2004, pp. 355–368.

[9] J. S. Parker, L. R. Moore, and K. T. Taylor, Accurate Computational Methods for Two-Electron Atom-Laser Interactions, *Optics-Express*, Vol. 8, 2001, pp. 436–441.

[10] L. Trefethen, *Spectral Methods in Matlab*, SIAM, Philadelphia, 2000.

[11] V. Veniard, R. Taieb, and A. Maquet, Photoionization of Atoms Using Time-Dependent Density Functional Theory, *Laser Physics*, Vol. 13, 2003, pp. 465–474.

[12] J. Zanghellini, M. Kitzler, C. Fabian, T. Brabec, and A. Scrinzi, Testing the Multi-Configuration Time-Dependent Hartree-Fock Method, *J. Phys. B: At. Mol. Phys.*, Vol. 37, 2004, pp. 763–773.

[13] J. Zanghellini, M. Kitzler, T. Brabec, and A. Scrinzi, An MCTDHF Approach to Multi-Electron Dynamics in Laser Fields, *Laser Physics*, Vol. 13, 2003, pp. 1064–1068.

Δt	abs. err	rel. err	time	fcount
2.00E-02	3.0671E-08	1.4902E-05	2	44032
1.00E-02	2.7000E-09	5.7671E-06	4	88024
5.00E-03	1.6183E-09	6.2495E-07	8	176048
2.50E-03	1.5052E-10	4.3914E-07	15	352064
1.25E-03	1.0370E-11	1.1871E-08	30	704072

Table 6: Performance of Runge-Kutta method, space discretization by pseudospectral method.

Δt	abs. err	rel. err	time	fcount
2.00E-02	4.5368E-06	1.1151E-03	1	22016
1.00E-02	1.1129E-06	2.7781E-04	2	44012
5.00E-03	2.7694E-07	6.9369E-05	4	88024
2.50E-03	6.9152E-08	1.7332E-05	8	176032
1.25E-03	1.7284E-08	4.3294E-06	15	352036
6.25E-04	4.3238E-09	1.0770E-06	30	704040

Table 7: Performance of variational splitting, space discretization by pseudospectral method.