

# Improved exponential split operator method for solving the time-dependent Schrödinger equation

André D. Bandrauk<sup>a</sup> and Hai Shen<sup>b</sup>

<sup>a</sup> *Département de Chimie, Faculté des Sciences, Université de Sherbrooke, Sherbrooke, Quebec, Canada J1K 2R1*

<sup>b</sup> *Département de Mathématique-Informatique, Faculté des Sciences, Université de Sherbrooke, Sherbrooke, Quebec, Canada J1K 2R1*

Received 12 September 1990; in final form 29 October 1990

A new method of splitting exponential operators is proposed in the exponential form of the operator solution of the time-dependent Schrödinger equation. The method is shown to be third-order accurate in the time increment. In particular the phase of the wavefunction is shown to be exceptionally accurate for time-independent potentials. The new method is shown to be more efficient than the standard second-order evolution operator algorithms for both time-independent and time-dependent potentials.

## 1. Introduction

Recent developments in laser physics and laser chemistry have pointed out the need for efficient algorithms to solve the time-dependent Schrödinger equation [1-4] and simultaneously the Maxwell-Schrödinger equation [5,6]. The first describes the quantum behaviour of matter in the presence of electromagnetic pulses whereas the second describes the classical propagation of electromagnetic pulses in molecular media. With present lasers, very intense fields are accessible so that nonperturbative methods are needed to solve the equations for the interaction of electromagnetic pulses with molecules [1].

The time-dependent Schrödinger equation describing molecular multiphoton transitions is a linear parabolic partial differential equation which can be written as

$$i\hbar \frac{\partial \psi_n}{\partial t}(\mathbf{R}, t) = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi_n}{\partial \mathbf{R}^2}(\mathbf{R}, t) + V_{nn}(\mathbf{R}) \psi_n(\mathbf{R}, t) + \sum_{n'} V_{nn'}(\mathbf{R}, t) \psi_{n'}(\mathbf{R}, t), \quad (1)$$

where  $V_{nn}(\mathbf{R})$  is the time-independent field free molecular (electronic) potential and  $V_{nn'}(\mathbf{R}, t)$  is the time-dependent electromagnetic-molecule interaction,

$$V_{nn'}(\mathbf{R}, t) = \boldsymbol{\mu}_{nn'}(\mathbf{R}) \cdot \mathbf{E}(\mathbf{r}, t). \quad (2)$$

$\mathbf{R}$  is a molecular coordinate whereas  $\mathbf{r}$  is the electromagnetic field coordinate.  $\mathbf{E}(\mathbf{r}, t)$  represents the electromagnetic pulse,  $\boldsymbol{\mu}_{nn'}(\mathbf{R})$  is a transition moment representing transitions between different electronic states of quantum number  $n$ . Solution of eq. (1) generates the total time-dependent molecular wavefunction  $\psi(\mathbf{R}, t, \mathbf{E}(\mathbf{r}, t))$  which becomes an implicit functional of the electric field  $\mathbf{E}$ . This function allows one in principle to calculate the exact total polarizability  $P(t, \mathbf{E}(\mathbf{r}, t))$  induced by the electromagnetic perturbation [5,6],

$$P(t, \mathbf{E}(\mathbf{r}, t)) = \langle \psi(\mathbf{R}, t, \mathbf{E} | \boldsymbol{\mu}(\mathbf{R}) | \psi(\mathbf{R}, t, \mathbf{E}) \rangle, \quad (3)$$

where  $\boldsymbol{\mu}$  is the total dipole moment of the system. The polarizability becomes a source term in Maxwell's equation,

$$\nabla^2 E(\mathbf{r}, t) - \frac{1}{c^2} \frac{\partial^2 E(\mathbf{r}, t)}{\partial t^2} = \frac{4\pi}{c^2} \frac{\partial^2 P(\mathbf{r}, t)}{\partial t^2}. \quad (4)$$

Eqs. (1) and (4) are the Maxwell-Schrödinger equation of a molecular system, the solution of which would enable one to describe nonlinear optical phenomena at the molecular level [5-7].

In the case of a slowly varying envelope, eq. (4) can be reduced to a nonlinear parabolic partial differential equation (the paraxial wave equation)

[5,6,8]. Thus both equations, (1) and (4) become diffusion equations with imaginary diffusion coefficients, the first being a linear and the second a nonlinear parabolic differential equation. For intense pulses, i.e. if the nonperturbative regime applies, both equations (1) and (4) must be solved accurately for long propagation times. In the present note we wish to present a new scheme for solving numerically the linear parabolic equation (1) to high order by split exponential operator methods. As shown by previous authors, the imaginary diffusion coefficient in the Schrödinger equation can render certain well known unstable numerical schemes such as explicit integration methods stable [8]. We extend here the previous work of Burstein and Mirin [9,10] for real hyperbolic initial value problems. The new higher order splitting method should be applicable to both linear real and imaginary diffusion equations. For nonlinear equations, the present method can be also implemented in the split step methods for solving such nonlinear equations [11]. We are currently pursuing these approaches.

## 2. Third-order split operator method

The exponential representation of the operator solution to the Schrödinger equation for a *time-independent* Hamiltonian has an exact formal solution in terms of the evolution operator [12]. Thus writing the one-dimensional time-dependent Schrödinger equation as (we set  $\hbar = m = 1$ ),

$$i \frac{\partial \psi(x, t)}{\partial t} = \left( -\frac{1}{2} \frac{\partial^2}{\partial x^2} + V(x) \right) \psi(x, t) \\ = (A+B)\psi(x, t), \\ A = -\frac{1}{2} \frac{\partial^2}{\partial x^2}, \quad B = V(x), \quad (5)$$

we can write the exact formal solution of (5) as

$$\psi(x, t + \Delta t) = \exp[-i\Delta t(A+B)]\psi(x, t). \quad (6)$$

This solution is no longer exact for a time-dependent  $V(x, t)$  as occurs in eq. (2) due to the noncommutativity of the now time-dependent Hamiltonian at different times [12]. Splitting of the exact formal exponential operator for the time-independent operator  $B = V(x)$ ,

$$S_{\text{ex}}(A, B) = \exp[\lambda(A+B)], \quad (7)$$

is the key problem in obtaining accurate numerical solutions to eq. (6) for propagation to the time  $t_n = n\Delta t + t$ . The simplest splitting formula is to first-order accuracy,

$$S_{\text{ex}}(A, B) = S_1(A, B, \lambda) + \frac{1}{2}[A, B]\lambda^2 + \dots, \quad (8)$$

where

$$S_1(A, B, \lambda) = \exp(\lambda A) \exp(\lambda B). \quad (9)$$

Here we use the notation of ref. [9]. Second-order accuracy is obtained with a *three-split-operator* symmetric decomposition [9,10],

$$S_2(A, B, \lambda) = \exp(\lambda A/2) \exp(\lambda B) \exp(\lambda A/2), \quad (10)$$

since one can show readily that

$$S_{\text{ex}} = S_2 + S' + O(\lambda^4), \\ S' = \frac{1}{24}[A + 2B, [A + B]]\lambda^3. \quad (11)$$

Eq. (10) can be written as an iteration of  $S_1$ ,

$$S_2(A, B, \lambda) = S_1(A, B, \lambda/2) S_1(B, A, \lambda/2). \quad (12)$$

This operator decomposition (i.e. (10) or (12)) is currently being used extensively in the chemical physics literature [3,13–15]. A third-order symmetric operator, by analogy to eq. (12), i.e.

$$S_3(A, B, \lambda) = S_2(A, B, \lambda/4) S_2(B, A, \lambda/4), \quad (13)$$

can be shown to be *asymptotically* accurate to third order [9,10], i.e. by iteration

$$S_3^N = [S_2(A, B, \lambda/N) S_2(B, A, \lambda/N)]^{N/4}, \quad (14)$$

one obtains third-order accuracy only in the limit  $N \rightarrow \infty$ . This requires many calculations per time step and hence is not practical.

Consecutive combinations of *five* operators can be obtained to give third-order accuracy by choosing a nonsymmetric generalization of (13),

$$S_3 = S_2(A, B, \gamma\lambda) S_2(A, B, \lambda(1-\gamma)), \\ \gamma = \frac{1}{2}(1 \pm i/\sqrt{3}). \quad (15)$$

Unfortunately, since  $\lambda = -i$  in the time-dependent Schrödinger equation, this new splitting with complex  $\gamma$ s creates exponentially growing and damped

solutions at different time steps, so that unitarity is not always conserved. Indeed numerical tries showed this scheme to be unstable, in spite of the promise of third-order accuracy. This scheme should be therefore useful for real partial differential equations.

We turn now to more general decompositions of the type encountered in eq. (10), as symmetric generalizations of (15),

$$S_3 = S_2(A, B, \gamma\lambda) S_2(A, B, \lambda(1-2\gamma)) S_2(A, B, \gamma\lambda) \\ = S_2(\gamma\lambda) S_2(\lambda(1-2\gamma)) S_2(\gamma\lambda). \quad (16)$$

Inserting  $S_2$  from (10) into (16) one obtains by comparison with the exact exponential operator

$$S_{\text{ex}}(A, B) = S_3 + S'(2\gamma^3 + (1-2\gamma)^3) + O(\lambda^4), \quad (17)$$

where  $S'$  is defined in eq. (11). For values of  $\gamma$  satisfying the condition

$$2\gamma^3 + (1-2\gamma)^3 = 0, \quad \gamma = 1/(2-2^{1/3}), \quad (18)$$

one obtains therefore a third-order accurate exponential operator  $S_3$  from eq. (18). The operator  $S_3$  preserves unitarity of the Schrödinger equation at every time iteration step. This is to be compared with the best third-order operator asymptotic  $S_3^N$ , eq. (14), which is third-order accurate only in the limit  $N \rightarrow \infty$ . Continuing the iteration processes in (16), i.e. next defining the exact evolution operator  $S_{\text{ex}}$  in terms of symmetric products of  $S_3$  would give

$$S_{\text{ex}}(AB) = S_3(\gamma\lambda) S_3(\lambda(1-2\gamma)) S_3(\lambda\gamma) \\ + T(2\gamma^4 + (1-2\gamma)^4) + O(\lambda^5), \quad (19)$$

where  $T$  is some remnant combination of commutators of  $A$  and  $B$ . The condition necessary for a fourth-order accurate  $S_4$ ,

$$2\gamma^4 + (1-2\gamma)^4 = 0, \quad (20)$$

has no real roots. Thus as in the case of the five-operator expression, eq. (15), complex roots would not preserve unitarity in the iteration steps, thus creating an unstable scheme. In fact, one can generalize eq. (19) to express  $S_n$  as products of three  $S_{n-1}$ , as shown recently by Suzuki [16] in the context of path integral calculations. However, these higher order  $S_n$ , i.e.  $n > 4$ , depend on  $S_4$  because of the recursion (19). Thus such higher order schemes would not be useful because of the violation of unitarity in  $s_4$ . We conclude therefore that eq. (16) seems to be the sim-

plest new third-order accurate splitting of operators. A final expression can now be written as

$$S_3(A, B, \lambda) = \exp(\gamma\lambda A/2) \exp(\gamma\lambda B) \\ \times \exp[\frac{1}{2}(1-\gamma)\lambda A] \exp[(1-2\gamma)\lambda B] \\ \times \exp[\frac{1}{2}(1-\gamma)\lambda A] \exp(\gamma\lambda B) \exp(\gamma\lambda A/2), \quad (21)$$

with  $\gamma$  given by eq. (19). Although this expression involves seven exponential operators, we will show in section 3 that numerical algorithms based on the third-order accurate equation (21) are more efficient than algorithms based on the standard second-order accurate evolution operator  $S_2$ , eq. (10).

### 3. Numerical comparisons

Eq. (10) gives the most widely used three-split-operator expression which is second-order accurate. Eq. (21) is the new third-order accurate scheme. As with the second-order method, this new seven-split-operator scheme preserves unitarity at all time steps. Second-order and third-order accuracy hold only for time-independent potentials  $B$ , eq. (5), as shown above. For time-dependent Hamiltonians, i.e. time-dependent potentials  $B = V(x) + f(x, t)$ , one can show by detailed calculation that the scheme based on  $S_3$ , eq. (21), remains third-order accurate [17]. This will be further corroborated by the calculations reported below.

For comparing the truncation errors in the two schemes (10) and (21), we shall use both the time-independent and time-dependent harmonic oscillator, i.e.  $B = x^2$  and  $x^2 + xf(t)$ . Exact solutions are known for both cases [18]. For the time-independent harmonic oscillator, one can obtain another third-order accurate evolution operator  $S'_3$  based on  $S_1$ , eq. (9), and  $S'$ , eq. (11), i.e.

$$S_{\text{ex}}(A, B) = S'_3(A, B, \lambda) + O(\lambda^4), \\ S'_3 = S_1(A, B, \lambda/2) \exp(S') S_1(A, B, \lambda/2), \\ \exp(S') = \exp(-\lambda^3 A/6) \exp(\lambda^3 B/3) + O(\lambda^4). \quad (22)$$

Thus for the time-independent harmonic oscillator, we shall compare three methods based on  $S_2$ ,  $S'_3$  and  $S_3$  respectively (table 1).

For the time-dependent harmonic oscillator,  $S'_3$ ,

Table 1

Maximum errors in time-independent ( $V(x)=x^2$ ) solution  $\psi(x, t)=\rho(x)\exp[i\phi(t)]$ ;  $-7\pi\leq x\leq 7\pi$ . CPU seconds in parentheses;  $t=600$  ( $\approx 100$  cycles)

	$S_2$	$S'_3$	$S_3$
$\Delta t=0.03$			
$\rho(x)$	$0.85\times 10^{-2}$	$0.84\times 10^{-5}$	$0.25\times 10^{-4}$
$\phi(t)$	$0.32\times 10^{-1}$ (405)	$0.55\times 10^{-4}$ (904)	$0.11\times 10^{-3}$ (1164)
$\Delta t=0.08$			
$\rho(x)$	$0.93\times 10^{-1}$	$0.31\times 10^{-3}$	$0.11\times 10^{-2}$
$\phi(t)$	0.23 (157)	$0.13\times 10^{-2}$ (345)	$0.47\times 10^{-2}$ (443)

Table 2

Maximum errors in time-dependent ( $V(x, t)=x^2+x\sin t$ ) solution  $\psi(x, t)=\rho(x, t)\exp[i\phi(x, t)]$ ;  $-7\pi\leq x\leq 7\pi$ . CPU seconds in parentheses;  $t=600$  ( $\approx 100$  cycles)

	$S_2$	$S_3$
$\Delta t=0.01$		
$\rho(x, t)$	$0.28\times 10^{-2}$	$0.23\times 10^{-5}$
$\phi(x, t)$	$0.16\times 10^{-1}$ (1259)	$0.13\times 10^{-2}$ (3404)
$\Delta t=0.03$		
$\rho(x, t)$	$0.25\times 10^{-1}$	$0.84\times 10^{-4}$
$\phi(x, t)$	0.14 (440)	$0.11\times 10^{-1}$ (1180)

eq. (22) is no longer valid due to noncommutativity of  $H(t)=A+B$  at different times [12]. Thus only  $S_2$  and  $S_3$  algorithms can be compared (table 2). The numerical calculations were performed by iterating the successive exponentials in  $S_2, S_3, S'_3$ . The kinetic operator  $A=-\frac{1}{2}\partial^2/\partial x^2$  was calculated by fast Fourier transform techniques. These are most convenient due to the well behaved properties of the potentials  $V(x), V(x, t)$  and functions  $\psi(x, t)$ . Spectral methods are known to have, in principle, infinite order accuracy in the space discretization ( $x$ ) for smooth solutions [19].

For computational purposes, functions  $\psi(x, t)$  based on the evolution operators  $S_2, S_3$  and  $S'_3$  were calculated for the time-independent harmonic oscillator ( $\omega=\sqrt{2}$ ) (table 1) and the same oscillator perturbed by a sinusoidal potential  $V(x, t)=x\sin t$ , i.e. with frequency  $\omega_0=1$  (table 2). The initial con-

ditions were chosen to be the ground state:  $\psi(x, 0)=\psi_{v=0}(x)=(\sqrt{2}/\pi)^{1/4}\exp(-x^2)$ . Numerical solutions were compared to the exact solution [18]. For the time-independent problem,  $\psi(x, t)=\rho(x)\exp[i\phi(t)]$ , the amplitude  $\rho$  depends on the space coordinate ( $x$ ) only whereas the phase  $\phi$  depends only on time ( $\phi=\omega t/2$ ). In the general case, i.e. for time-dependent potentials, both  $\rho$  and  $\phi$  depend on  $x$  and  $t$ . Tables 1 and 2 present the maximum differences between the numerical and exact values of the amplitude and phase. All calculations were performed on a RISC 6000/model 530 IBM workstation (10 megaflop performance). Calculation times are reported in CPU seconds for such a machine.

A study of tables 1 and 2 shows that the third-order accurate evolution operator  $S_3$ , eq. (21), is superior in accuracy to results obtained with the standard second-order operator  $S_2$ , eq. (10). Thus for equal computational time (e.g.  $S_3(\Delta t=0.08)$  versus  $S_2(\Delta t=0.03)$ , table 1),  $S_3$  gives always better accuracy in the amplitude by about one order of magnitude than  $S_2$  for both time-independent and time-dependent problems. In particular,  $S_3$ , which compares well with  $S'_3$ , gives more accurate phases (by at least one order of magnitude) than  $S_2$  for the time-independent problem. For the time-dependent problem, table 2 shows that  $S_3$  gives a superior amplitude and a slightly better phase than  $S_2$ . Clearly, phase is a very sensitive function of the potential.

In conclusion, we have shown that the new evolution operator  $S_3$ , eq. (21), allows explicit exponential numerical integration of parabolic partial differential equations such as the time-dependent Schrödinger equation with third-order accuracy, i.e. errors depend on  $(\Delta t)^4$ , where  $\Delta t$  is the time step. For time-independent potentials, the method gives more accurate phases than the second-order  $S_2$ . Since bound states and resonances (quasi bound states) are strongly dependent on phases [14,20], this higher order evolution operator should serve as a useful tool for determining accurate spectra of time-independent systems. The present method is therefore superior in accuracy over the standard second-order algorithms based on  $S_2$ . We are currently extending this new method to the linear coupled equations (1) which occur in intense field multiphoton electronic transitions and to the accompanying Maxwell equa-

tion (4) which is a nonlinear equation.

### Acknowledgement

We thank the Natural Sciences and Engineering Research Council of Canada for grants supporting this work. We also like to thank M. Suzuki for communicating the result of ref. [16] prior to publication.

### References

- [1] A.D. Bandrauk, ed., NATO ASI Series, Vol. B171. Atomic and molecular processes with short intense laser pulses (Plenum Press, New York, 1988).
- [2] K.C. Kulander, Phys. Rev. A 38 (1988) 778.
- [3] R. Heather and H. Metiu, J. Chem. Phys. 86 (1987) 5009.
- [4] H.W. Lee and T.F. George, J. Phys. Chem. 83 (1979) 929.
- [5] S. Chelkowski and A.D. Bandrauk, J. Chem. Phys. 89 (1988) 3618.
- [6] B.W. Shore and K.C. Kulander, J. Mod. Opt. 36 (1989) 857.
- [7] Y.R. Shen, The principles of nonlinear optics (Wiley, New York, 1984).
- [8] A. Askar and A.S. Cakmak, J. Chem. Phys. 68 (1978) 2794.
- [9] S.Z. Burstein and A.A. Mirin, J. Comput. Phys. 5 (1970) 547.
- [10] Q. Sheng, IMA J. Numer. Anal. 9 (1989) 199.
- [11] R.H. Hardin and F.D. Tappert, SIAM Rev. Chronicle 15 (1973) 423.
- [12] P. Pechukas and J.C. Light, J. Chem. Phys. 44 (1966) 3897.
- [13] P.L. DeVries, in: NATO ASI series, Vol. B171. Atomic and molecular processes with short intense laser pulses, ed. A.D. Bandrauk (Plenum Press, New York, 1988), pp. 113-117.
- [14] M.D. Feit, J.A. Fleck Jr. and A. Steiger, J. Comput. Phys. 47 (1982) 412.
- [15] M. Suzuki, J. Math. Phys. 26 (1985) 601.
- [16] M. Suzuki, J. Math. Phys., submitted for publication.
- [17] H. Shai and A.D. Bandrauk, to be published.
- [18] H. Husimi, Progr. Theoret. Phys. 9 (1953) 381.
- [19] S. Osher, in: Spectral methods for partial differential equations, eds. R.G. Voigt, D. Gottlieb and M.Y. Hussaini (SIAM Publications, Philadelphia, 1984) p. 209.
- [20] A.D. Bandrauk and O. Atabek, in: Advances in chemical physics, Vol. 73. Lasers, molecules, methods, eds. J.O. Hirschfelder, R.E. Wyatt and R.D. Coalson (Wiley, New York, 1989) ch. 19; J. Phys. Chem. 91 (1987) 6469.