Precise integration for the time-dependent Schrödinger equation*

Suying Zhang¹, Jiangdan Li
Institute of Theoretical Physics, Shanxi University, Taiyuan, 030006, P R China
E-mail address: zhangsy@sxu.edu.cn

Abstract. The precise integration method proposed for linear-invariant dynamical system can give precise numerical result approaching to the exact solution at the integration points. In this paper, a cheap and easy to implement precise integration method for time-dependent Schrödinger equation with periodic Hamiltonians is presented based on Magnus expansion of the solution of the system. The method requires evaluation of only one exponential of matrix, and preserves many of the qualitative properties of the exact solution.

1. Introduction
In this work we present new geometric integrators for solving the Schrödinger equation (\( H = \hbar \))

\[
\begin{cases}
   i \frac{d}{dt} \psi(x,t) = \hat{H}(p,x,t)\psi(x,t) \\
   \psi(x,t_0) = \psi_0(x)
\end{cases}
\]

where \( \psi(x,t) \) is the wave function associated with the system, \( p = -i \frac{\partial}{\partial x} \) and \( \hat{H}(p,x,t) \) is a Hermitian Hamiltonian operator governing the evolution of the system. After spatial discretization the Schrödinger equation can be considered as linear ordinary differential equations. In most cases, the Schrödinger equations have periodic Hamiltonians, and after averaging of the time-dependent part of the Hamiltonian over its period, the system can be considered as linear-invariant. So precise integration method [1-3] can be used for solving the linear-invariant system. In the following we will present the new numerical methods. In the end the performance of the methods is illustrated with several examples.

2. Spatial discretization and the Magnus series solution of the time-dependent Schrödinger equation

*Supported by National Natural Science Foundation of China (10472059)
¹ To whom any correspondence should be addressed.
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 of length $\Delta x = (x_f - x_0) / N$ and consider $c_n = \psi(x_n, t)$, where $x_n = x_0 + n\Delta x$, $n = 1, 6, N$, thus obtaining the finite dimensional linear equation

$$i \frac{d}{dt} c(t) = H(t)c(t), \quad c(0) = c_0$$

(2)

where $c = (c_1, c_6, c_N)^T \in \mathbb{C}^N$ and $H \in \mathbb{C}^{N \times N}$ is an Hermitian matrix associated to the Hamiltonian (usually it is real and symmetric).

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:

$$\frac{d}{dt} \begin{bmatrix} \mathbf{q} \\ \mathbf{p} \end{bmatrix} = J \otimes H(t) \begin{bmatrix} \mathbf{q} \\ \mathbf{p} \end{bmatrix}$$

(3)

with

$$J \otimes H(t) = \begin{bmatrix} 0 & H(t) \\ -H(t) & 0 \end{bmatrix}.$$

(4)

where $\mathbf{q} = \text{Re } c$, $\mathbf{p} = \text{Im } c$ and the corresponding Hamiltonian function is $H = \frac{1}{2} \mathbf{p}H(t)\mathbf{p} + \frac{1}{2} \mathbf{q}H(t)\mathbf{q}$. This equation is usually related to the evolution of a classical Hamiltonian system with $\mathbf{q}$ and $\mathbf{p}$ being the coordinates and momentum. If we use the geometric integrations to solve it, some qualitative properties (symplecticity, unitary, time-symmetry, etc.) can be preserved.

From now we discuss the question in the interval $[t_k, t_{k+1}](t_k = t_0 + k\tau, \tau$ is the step-size of time). Noting $\overline{H}(t) = J \otimes H(t)$, the solution of equation (3) can be written as

$$\begin{bmatrix} \mathbf{q}_k \\ \mathbf{p}_k \end{bmatrix} = \exp \left( \int_{t_{k-1}}^{t_k} \overline{H}(s) ds \right) \begin{bmatrix} \mathbf{q}_{k-1} \\ \mathbf{p}_{k-1} \end{bmatrix}, \quad k = 1, 2, 6$$

(5)

It is the exact solution of equation (3) when the condition $\int_0^t [\overline{H}(s), \overline{H}(s)] ds = 0$ holds for all $t$, where $[\mathbf{A}, \mathbf{B}] = \mathbf{A}\mathbf{B} - \mathbf{B}\mathbf{A}$. This is not the usual case and in general one has to look for numerical approximate solutions. Magnus series methods [4-6] give 2n order approximate solution of the equation (3):

$$\begin{bmatrix} \mathbf{q}_k \\ \mathbf{p}_k \end{bmatrix} = \exp(\mathbf{\Omega}) \begin{bmatrix} \mathbf{q}_{k-1} \\ \mathbf{p}_{k-1} \end{bmatrix}, \quad k = 1, 2, 6$$

(6)

where $\mathbf{\Omega} = \sum_{k=1}^{N} \mathbf{\Omega}_k$. Each term $\mathbf{\Omega}_k$ in the series is a multiple integral of combinations of nested commutators containing $\overline{H}(t)$, and it can be obtained in a recursive way [4-6].

3. Precise integration for the time-dependent Schrödinger equation
Precise integration method can compute the exponential matrix involved in the numerical methods quickly and effectively. As stated above, the approximate solution of the equation (3) is
\[
\begin{bmatrix}
q_k \\
p_k
\end{bmatrix} = \exp(\Omega) \begin{bmatrix}
q_{k-1} \\
p_{k-1}
\end{bmatrix}, \quad k = 1,2,6
\]
(7)
The exponential matrix \( \exp(\Omega) \) can be calculated precisely as follows. That is,
\[
\exp(\Omega) = \left[\exp(\Omega / m)\right]^m
\]
with \( m = 2^L \). Let \( L=20 \), we have \( m=1048576 \).
\[
\exp(\Omega / m) \approx I + \frac{1}{m} \Omega + \frac{1}{2} \left( \frac{1}{m} \Omega \right)^2 + \frac{1}{6} \left( \frac{1}{m} \Omega \right)^3 + \frac{1}{24} \left( \frac{1}{m} \Omega \right)^4 = I + T_a
\]
(9)
with
\[
T_a = \frac{1}{m} \Omega + \frac{1}{2} \left( \frac{1}{m} \Omega \right)^2 + \frac{1}{6} \left( \frac{1}{m} \Omega \right)^3 + \frac{1}{24} \left( \frac{1}{m} \Omega \right)^4
\]
(10)
where \( T_a \) is a small quantity of matrix. So we have
\[
T = \exp(\Omega) = \left[I + T_a\right]^{2^L} = \left[I + T_a\right]^{2^{L-1}} \times \left[I + T_a\right]^{2^{L-1}}
\]
(11)
Noting
\[
(I + T_b) \times (I + T_c) = I + T_b + T_c + T_b \times T_c
\]
(12)
we can execute the following circulation
\[
\text{for ( iter = 0; iter < L; iter ++ ) } T_a = 2 \times T_a + T_a \times T_a
\]
(13)
then
\[
T = I + T_a
\]
(14)
If the Hamiltonian function is periodic, we can obtain arbitrary even-order approximate solution for time-dependent Schrödinger equation only by calculating this matrix \( T \). That is
\[
\begin{bmatrix}
q_k \\
p_k
\end{bmatrix} = T \begin{bmatrix}
q_{k-1} \\
p_{k-1}
\end{bmatrix}, \quad k = 1,2,6
\]
(15)
4. Numerical experiments
In order to appreciate the efficiency of the methods presented in this paper we will consider the Hamiltonian of a diatomic molecule with a linear time-dependent perturbation
\[
\hat{H} = -\frac{1}{2\mu} \frac{\partial^2}{\partial x^2} + \hat{V}(x) + \hat{xf}(t)
\]
(16)
where \( \mu \) is the reduced mass of the diatomic molecule. We consider the Morse potential, \( \hat{V}(x) = D(1 - e^{-\alpha x})^2 \), \( D \) being the dissociation energy and \( \alpha \) the length parameter. In particular we will study the HF molecule, whose parameters are \( \mu = 1745 \text{ a.u.}, \ D = 0.2251 \text{ a.u.}, \) and \( \alpha = 1.1741 \text{ a.u.} \). For the time-dependent perturbation we consider the interaction with a laser field:

\[
f(t) = A \cos(\omega t)
\]

for the following three cases:

\[
A = 0.0011025 \text{ a.u.} \quad w = 0.193w_0, \quad w_0 = \alpha \sqrt{2D/\mu}
\]

\[
A = 0.011025 \text{ a.u.} \quad w = 5w_0, \quad w_0 = \alpha \sqrt{2D/\mu}
\]

\[
A = 0.011025 \text{ a.u.} \quad w = 0.9476w_0, \quad w_0 = \alpha \sqrt{2D/\mu}
\]

As initial condition we take the ground state of the Morse oscillator, \( \psi_0(x) = \text{Re} \exp(-\beta x) \exp(-\gamma e^{-\alpha x}) \), with \( \gamma = 2D/w_0, \ \beta = (\gamma - 1/2)\alpha \) where \( R \) is the normalization constant. The grad for the spatial coordinate \( x \) ranges from \(-0.8\) to \(4.32\) with \( N = 64 \) with periodic boundary conditions assumed. Using fourth-order space discretization to the equation (3), we can obtain a classical time-dependent Hamiltonian problem. Then we use the fourth-order method stated above to solve it. The numerical results are shown in Figs. 1-6. We consider the laser field perturbation through 4000 periods of the laser frequency, and display the error of energy and norm of the numerical solution for the first case in Fig. 1, and for the second case in Fig. 2 with the period of the laser field as the time step. In Fig. 3 we give the error of energy and norm of the numerical solution for the third case with 14 times the period of the laser field as the time step, numerical results show that the methods allow big time-steps.

**Fig. 1** The error of energy and norm of the numerical solution for \( A = 0.011025 \text{ a.u.}, \ w = 0.193w_0 \) with the period of the laser field as the time step.

5. Conclusion
In this paper, we present a series of methods that lead to high accuracy computations of time-dependent Schrödinger equation with periodic Hamiltonians. We need to calculate only one exponential of matrix. The methods are very cheap, and the symplecticity and unitarity of the numerical solution are conserved to high order. Moreover the methods have better stability, allowing bigger time-steps, and have superiority if the time-dependent functions oscillate quickly.

![Fig. 2](image1.png)  
**Fig. 2** The error of energy and norm of the numerical solution for $A = 0.011025 \text{ a.u.}$, $w = 5w_0$ with the period of the laser field as the time step.

![Fig. 3](image2.png)  
**Fig. 3** The error of energy and norm of the numerical solution for $A = 0.011025 \text{ a.u.}$, $w = 0.9476w_0$ with 14 times the period of the laser field as the time step.

References

[1] Zhong W X 1994 *J. Dalian Univ. Technol.* **34(2)** 131-136  
[2] Zhong W X, Ouyang H J and Deng Z C Computational structural mechanics and optimal control 1993 (Dalian: Dalian University of Technology Press) p.269 (in Chinese)  
[3] Zhang S Y and Deng Z C 2003 *Mech. Res. Commun.* **30(1)** 33-38  
[4] Blanes S and Moan P C 2001 *J. Comput. Phys.* **170** (1) 205-230  
[5] Magnus W 1954 *Commun. Pure Appl. Math.* **7** 649-673  
[6] Blanes S, Casas F and Ros J 2002 *BIT* **42(2)** 262-284  
[7] Blanes S, Casas F and Ros J 2000 *BIT* **40(3)** 434-450  
[8] Iserles A and Norsett S P *Phil. Trans. R. Soc., Lond.* A **357** 983-1019