

# An accurate and efficient scheme for propagating the time dependent Schrödinger equation

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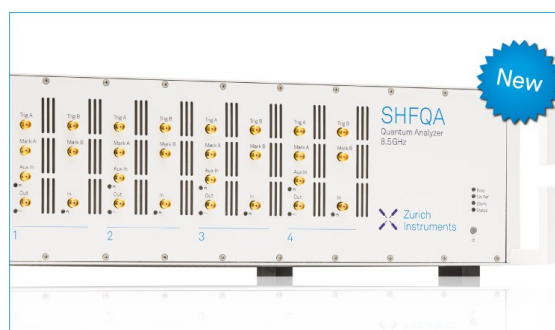
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# An accurate and efficient scheme for propagating the time dependent Schrödinger equation

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A new propagation scheme for the time dependent Schrödinger equation is based on a Chebychev polynomial expansion of the evolution operator  $\hat{U} = \exp(-i\hat{H}t)$ . Combined with the Fourier method for calculating the Hamiltonian operation the scheme is not only extremely accurate but is up to six times more efficient than the presently used second order differencing propagation scheme.

## I. INTRODUCTION

In the field of molecular dynamics, quantum mechanical time dependent calculations are emerging as an important tool in the construction of models and simulations of molecular encounters.<sup>1-10</sup> The main advantage of time dependent calculations is the ease of implementation and more important, the ease of interpretation. Many intimate details of the collision process can be revealed by examining the time propagation of the wave packet. From the point of view of accuracy time dependent methods until now have not been comparable to stationary coupled channel calculations.<sup>11</sup>

In this work a new time dependent propagation scheme is presented which has the desired accuracy. Wave packets can be propagated for long durations with the accuracy limited only by the precision of the computer. Moreover, the numerical procedure is up to six times more efficient than existing propagation schemes.

In quantum mechanics the state of the system is represented by the wave function  $\psi$ , while the time evolution is governed by the Schrödinger equation

$$i \frac{d\psi}{dt} = \hat{H}\psi \quad (1.1)$$

(in this work atomic units are used). A numerical construction of a solution the time dependent Schrödinger equation follows three stages. First the wave function  $\psi$  is discretized by representing it on grid points (values of  $\psi$  between grid points are obtained by interpolation). Secondly the Hamiltonian operator

$$\hat{H} = \frac{\hat{p}^2}{2m} + \hat{V} \quad (1.2)$$

and its operation on  $\psi$ ,  $\hat{H}\psi$  has to be calculated. The main difficulty in such an operation arises from the kinetic energy operator because of its nonlocal character. McCullough and Wyatt<sup>1</sup> and later Kulander<sup>2</sup> and Askar and Cakmak<sup>3</sup> approximated the kinetic energy operator using a finite difference scheme. **The drawback of the finite difference method is its low accuracy and slow rate of convergence,** due to the semilocal approximation to the kinetic energy. With the in-

troduction of the Fourier method, this difficulty has been eliminated.<sup>6,7,12</sup> In the Fourier method the kinetic energy is calculated in  $p$  space. This is done by a discrete Fourier transform then the transformed wave function is multiplied by  $-k^2$ . The operation is completed by transforming back to configuration space using an inverse Fourier transform. It has been shown<sup>7</sup> that the commutation relations of quantum mechanics  $[\hat{p}, f(x)] = i f'(x)$  are preserved in the discrete representation. This means that for band limited wave functions, the accuracy of the Fourier method in calculating the Hamiltonian operation is limited only by the precision of the computer. A detailed description of the Fourier method can be found elsewhere.<sup>7</sup>

The third step is to propagate the wave function in time. The general solution of Eq. (1.1) has the form

$$\psi(t+dt) = \exp(-i\hat{H}dt)\psi(t). \quad (1.3)$$

The simplest scheme for propagating Eq. (1.1) is to expand the evolution operator  $\hat{U} = \exp(-i\hat{H}dt)$  in a Taylor series:

$$\exp(-i\hat{H}dt) = 1 - i\hat{H}dt + \dots \quad (1.4)$$

It has been found that a numerical scheme based on this expansion is not stable. This comes about because the scheme does not conserve the time reversal symmetry of the Schrödinger equation. With a symmetric modification of the expansion stability is reached. One way to formulate the scheme is to use second order differencing (SOD) to approximate the time derivative in Eq. (1.1). Another formulation uses the symmetric relation:

$$\psi(t+dt) - \psi(t-dt) = (e^{-i\hat{H}dt} - e^{i\hat{H}dt})\psi(t) \quad (1.5)$$

and then by expanding  $\hat{U} = \exp(-i\hat{H}dt)$  and  $\hat{U}^\dagger$  in a Taylor series the explicit second order propagation scheme is obtained:

$$\psi(t+dt) = \psi(t-dt) - 2idt\hat{H}\psi(t). \quad (1.6)$$

This is the time propagation scheme used in the finite difference method of Askar and Cakmak<sup>3</sup> and also in the Fourier method.<sup>7</sup> There are other existing explicit and implicit propagation schemes based on a Taylor expansion of the evolution operator  $\hat{U}$ .<sup>1</sup> In all of these propagations, for long duration times, the basic propagation scheme must be repeated

many times. Although the second order differencing propagation scheme (SOD) conserves the norm and energy, errors will accumulate in the phase, putting a restriction on the accuracy. To overcome these difficulties, a new propagating scheme is presented, in which the evolution operator  $\hat{U}$  is expanded in a Chebyshev series:

$$e^{(-i\hat{H}dt)} \approx \sum_{n=0}^N a_n \varphi_n(-i\hat{H}dt), \quad (1.7)$$

where  $a_n$  are the expansion coefficients and  $\varphi_n$  are the complex Chebyshev polynomials. Because of the uniform character of the Chebyshev expansion the error decreases exponentially once  $N$  is large enough. This means that the error in propagation can be kept lower than the round-off error imposed by the computer. Considering that in using the Fourier method errors in the Hamiltonian operation can be kept in check, the combined method has an error determined only by hardware considerations.

## II. THE CHEBYCHEV METHOD

The strategy chosen for the propagation scheme is to expand the evolution operator  $\hat{U} = \exp -i\hat{H}dt$  in a polynomial series in the operator:  $-i\hat{H}dt$ . The problem then becomes a choice of the best polynomial approximation for this series. It has been shown<sup>13</sup> that this problem reduces to approximating the scalar function  $e^z$  by a polynomial expansion where  $z$  belongs to the domain which includes all the eigenvalues of the operator  $-i\hat{H}dt$ . It is known<sup>13</sup> that the best approximation is achieved by an expansion based on the complex Chebyshev polynomials  $\varphi_k$ . (The reason is the uniform character of the complex Chebyshev polynomials in distributing the errors in the interval  $[-i, i]$ . These polynomials are a complex version of the Chebyshev polynomials defined as

$$\varphi_k(\omega) = T_k(-i\omega), \quad \omega \in [-i, i] \quad (2.1)$$

and the  $T_k$  are the Chebyshev polynomials.  $\varphi_k$  are orthogonal on the imaginary interval  $[-i, i]$  with respect to the following inner product:

$$\langle f, g \rangle = -i \int_{-i}^i \frac{f(\omega)g^*(\omega)}{\sqrt{1-|\omega|^2}} d\omega. \quad (2.2)$$

The domain of the eigenvalues of the Hamiltonian  $\hat{H} = \hat{p}^2/(2m) + \hat{V}$  depends on the discretization scheme. In the Fourier method the eigenvalues are real because the Hamiltonian is Hermitean.<sup>7</sup> The domain of the eigenvalues can be estimated as follows. The maximum momentum  $P_{\max}$  represented on the grid, is defined by the grid size  $\Delta x$ :

TABLE I. Numerical effort vs accuracy for the  $n = 1$  and  $n = 4$  states of the harmonic oscillator.  $t = 5$  periods,  $dx = 0.32$ , and 32 spatial grid points.

$n = 0$				$n = 4$		
N	Norm	Energy	Error	Norm	Energy	Error
160	1.032 869	0.490 875	$0.404 \times 10^{-3}$	1.017 712	4.036 769	$0.652 \times 10^{-3}$
168	0.999 259	0.522 325	$0.272 \times 10^{-6}$	1.000 233	4.493 902	$0.986 \times 10^{-6}$
176	0.999 968	0.500 936	$0.295 \times 10^{-9}$	0.999 989	4.500 270	$0.393 \times 10^{-6}$
183	1.000 000	0.499 973	$0.111 \times 10^{-10}$	1.000 000	4.499 998	$0.393 \times 10^{-6}$
191	1.000 000	0.499 980	$0.111 \times 10^{-10}$	1.000 000	4.499 996	$0.393 \times 10^{-6}$

$$P_{\max} = \frac{\pi}{\Delta x}. \quad (2.3)$$

From Eq. (2.3) the maximum kinetic energy is  $P_{\max}^2/(2m)$ . If the minimum of the potential (represented on the grid) is  $V_{\min}$  and its maximum  $V_{\max}$ , the range of the eigenvalues of  $\hat{H}$  is

$$\lambda \in \left[ V_{\min}, V_{\max} + \frac{\pi^2}{2m\Delta x^2} \right]. \quad (2.4)$$

The scalar function  $z$  is chosen to be in the range of  $i\lambda dt$ . Defining

$$R = \frac{dt \left( \frac{\pi^2}{2m\Delta x^2} + V_{\max} - V_{\min} \right)}{2}, \quad G = V_{\min} dt$$

and

$$\omega = \frac{[z - i(R + G)]}{R}$$

one obtains:

$$e^z = e^{i(R+G)} e^{R\omega} \omega \in [-i, i]. \quad (2.5)$$

At this step  $e^z$  is expanded in the Chebyshev series

$$e^z \approx \sum_{k=0}^N a_k \varphi_k(\omega), \quad (2.6)$$

where

$$a_k = -ie^{i(R+G)} \int_{-i}^i \frac{e^{R\omega} \varphi_k(\omega)}{\sqrt{1-|\omega|^2}} d\omega = e^{i(R+G)} C_k J_k(R) \quad (2.7)$$

and  $C_k = 1$  for  $k = 1$  and  $C_k = 2$  for  $k > 1$ .  $J_k$  are Bessel functions of the first kind of order  $k$ . The high accuracy of this expansion can be traced to the fact that when  $k$  is greater than  $R$ ,  $J_k(R)$  goes to zero exponentially fast. Thus the degree  $N$  of the expansion has to be at least  $R$ . In this work  $N$  was chosen to be  $\alpha R$  where  $\alpha > 1$ . The value of  $\alpha$  depends on the degree of accuracy needed and can be chosen to bring errors below the accuracy of the computer. The propagation scheme is obtained by substituting  $-i\hat{H}dt$  for  $z$  in Eq. (2.6) and using Eq. (2.7):

$$\hat{U}(dt) \approx \sum_{k=0}^N a_k \varphi_k \left( \frac{-i\hat{H}dt}{R} \right), \quad (2.8)$$

where the Chebyshev polynomials in the operator  $i\hat{H}dt$  are computed by the recurrence relation satisfied by the polynomials  $\varphi_k(\hat{X})$ :

$$\varphi_k(\hat{X}) = 2\hat{X}\varphi_{k-1}(\hat{X}) + \varphi_{k-2}(\hat{X}) \quad (2.9)$$

and

$$\varphi_0(\hat{X}) = 1, \quad \varphi_1(\hat{X}) = \hat{X},$$

TABLE II. Comparison of accuracy and numerical effort between the Chebychev and second order differencing time propagation scheme.  $n = 4$ .

		CH1	CH2	SOD1	SOD4
$t = 1$	$N^a$	39	61	61	244
	Error	$0.501 \times 10^{-5}$	$0.469 \times 10^{-6}$	$0.212 \times 10^{-4}$	$0.530 \times 10^{-6}$
$t = 3$	$N$	119	183	183	732
	Error	$0.451 \times 10^{-6}$	$0.451 \times 10^{-6}$	$0.169 \times 10^{-3}$	$0.983 \times 10^{-6}$
$t = 25$	$N$	962	1525	1525	6100
	Error	$0.443 \times 10^{-6}$	$0.433 \times 10^{-6}$	$0.103 \times 10^{-1}$	$0.403 \times 10^{-4}$

<sup>a</sup>  $N$  is the number of calls to the Hamiltonian during the propagation. CH1 is the Chebychev scheme  $N$  is 1.3 times the stability limit. CH2 is the Chebychev scheme  $N$  is 2.0 times the stability limit. SOD1 is second order differencing with a time step close to the stability limit. SOD4 is second order differencing with a time step of 1/4 of the stability limit.

where  $\hat{X}$  is the operator  $(-i\hat{H}dt)/R$ . The basic algorithm is then used as a one step propagator obtaining the solution at the final time  $t + dt$  directly from the initial data, or as a marching scheme if one is interested in intermediate results. The size of the time step  $dt$  depends only on the information one wants to get out of the numerical procedure.  $R$  and the order  $N$  are determined accordingly. The refinement of the scheme is then based on increasing the order of the expansion and not by decreasing the time step.

### III. EXAMPLES

#### A. The harmonic oscillator

In this example the Chebychev propagating scheme and the second order differencing (SOD) scheme are compared to analytic solutions of the Schrödinger equation for the harmonic oscillator. The harmonic oscillator has the Hamiltonian:

$$\hat{H} = \frac{\hat{p}^2}{2} + \frac{\hat{x}^2}{2}. \quad (3.1)$$

Propagating the eigenfunctions is a good test of the accuracy of the method. The analytic solution of this propagation at time  $t$  is

$$\psi_n(t) = \psi_n(0)e^{-i(n+1/2)t}, \quad (3.2)$$

$\psi_n$  is the harmonic oscillator eigenfunction and  $n$  is the index of the energy level.

Table I demonstrates the exponential convergence of the Chebychev expansion with increasing the order  $N$ . The error is estimated by the deviation from the analytic solution:

$$\text{error}(t) = \int |\psi_{\text{anal}}(x, t) - \psi_{\text{calc}}(x, t)|^2 dx, \quad (3.3)$$

where  $\psi_{\text{anal}}$  is the analytic result of Eq. (3.2) and  $\psi_{\text{calc}}$  is the propagated wave function. Unlike the SOD scheme the Chebychev scheme is not unitary. Therefore energy and norm are not conserved. This means that the error can also be estimated by the deviation of the energy and norm of the propagated wave function. In Table I  $N$  is the order of the Chebychev polynomial and also is the number of times the Hamiltonian operation is calculated. It can be seen that the errors decrease rapidly with the growth of  $N$  from  $N = 160$  to  $N = 183$ . From  $N = 183$  to  $N = 191$  the accuracy is saturated due to round off errors in the single precision floating point form used. For  $n = 4$  there are also errors in the Hamiltonian operation. Decreasing  $\Delta x$  and increasing the grid size to 64 suppresses the error in  $n = 4$  to  $0.323 \times 10^{-10}$ .

Table II compares the Chebychev propagation scheme

TABLE III. Summary of parameters used in the surface scattering calculations.

	CH	SOD	Explanations
m	7 343.4	7343.4	mass
dx	0.6475	0.6475	grid interval in x
dz	0.6475	0.6475	grid interval in z
dt	80 000.	50.	time step
N	580.	1600.	number of calls to the Hamiltonian
nx	64.	64.	number of grid points in x
ny	64.	64.	number of grid points in z
Potential parameters			
g	5.18	5.18	lattice constant
D	0.000 12	0.000 12	
$\alpha$	0.582	0.582	$V = De^{-\alpha x}[1 - 2\beta \cos[2\pi(x/g)]]$
$\beta$	0.05	0.05	
Initial wave function parameters			
z0	21.	21.	initial average position
Dz0	9.	9.	initial width
Pz0	— 3.42	— 3.42	initial momentum in z direction
Px0	0.	0.	initial momentum in x direction

TABLE IV. Comparison of scattering intensities for the He/W system between the Chebychev (CH), second order differencing (SOD), and coupled channel (CC) calculations.

Peak	CH	SOD	CC
0	0.862 818	0.858 475	0.862 073
1	0.068 297	0.067 652	0.068 670
2	0.000 292	0.000 300	0.000 291
3	0.000 000 66	<sup>a</sup>	<sup>a</sup>

<sup>a</sup> The results for the SOD and the CC calculations for peak 3 are below the relative numerical error so they were omitted. Peak 3 for the Chebychev scheme is five orders of magnitude above the numerical background of  $10^{-13}$ .

to the second order differencing (SOD) scheme. Certain points in Table II should be emphasized: First the Chebychev scheme unlike the SOD scheme does not accumulate errors, so that the error at  $t = 25$  periods is of the same order as at  $t = 1$ . In the SOD scheme on the other hand, errors accumulate linearly. Secondly, for long time durations the Chebychev scheme becomes six times more efficient than the SOD scheme for adequate accuracy. The reason is that in the SOD scheme, in order to eliminate numerical dispersion, the time step is chosen to be 1/4 to 1/5 of the stability limit.<sup>7</sup>

## B. Scattering from a surface

In this example a two dimensional scattering problem is solved and compared to a coupled channel calculation. A model of He scattering from a metal surface is used. The physical picture is of a plane wave hitting the surface and scattering into diffraction peaks. A time dependent calculation is a simulation of a pulsed experiment while a coupled channel calculation represents a cw experiment. To minimize the discrepancy between the stationary coupled channel method and the time dependent method due to the spread in energy in the wave packet, a very wide Gaussian initial wave packet in the  $z$  direction perpendicular to the surface was chosen. In the  $x$  direction the periodic boundary conditions were matched to a multiple of the unit cell. The potential was chosen the same as in Ref. 9 Table III summarizes the parameters used for the calculation. The results were compared at 80 000 a.u. of time after the collision had been completed. The order of the Chebychev scheme was  $N = 580$  compared to  $N = 1600$  (number of calls to the Hamiltonian) in the SOD method. Table IV compares the Chebychev scheme to the SOD scheme and to the CC results.<sup>9</sup> The CC method used is described in Ref. 14.

Because of the energy spread of the wave packet there are differences between the Chebychev results compared to the CC results. These differences are below the errors induced by the spread in the energy of the wave packet (the relative spread in energy was  $1.06 \times 10^{-3}$ ). Peak 3 was not resolved in the CC calculation. These differences are a manifest of the time energy uncertainty principle. Considering that a typical spread in energy of experimental beams is of the order of  $10^{-2}$ , the energy spread of this time dependent calculation is lower than the experimental spread. Comparing the Chebychev scheme to the SOD scheme, the SOD scheme is an order of magnitude less accurate; this could be improved by decreasing the time step to 1/4 of the stability limit. Another check of accuracy is to compare the ampli-

tudes of the diffraction peaks to the background. In the CH scheme the background is of the order of  $10^{-13}$  while in the SOD method the background is of the order of  $10^{-5}$ . Because of this the third diffraction peak in the SOD scheme cannot be resolved. Even if one is satisfied with the accuracy of the SOD scheme in Table IV, it represents approximately three times more numerical effort than the Chebychev scheme. In order to eliminate numerical dispersion and to improve the accuracy of the SOD scheme one needs approximately six times more numerical effort. The advantage of the Chebychev scheme is even more pronounced when trapping on the surface takes place. In this case long integration times are needed in order to obtain resonance lifetimes. Currently the Chebychev scheme is used for a 3D He/Pt scattering simulation.

## IV. CONCLUSIONS

The Chebychev propagation scheme is an important step in establishing time dependent wave packet methods as tools in molecular dynamics. Together with the Fourier method for calculating the Hamiltonian operation, an accurate and highly efficient general method is presented for solving the time dependent Schrödinger equation. One of the main advantages of this combined method is the slow increase in numerical effort with the increase in the size of the problem. As a function of  $M$  (the total number of grid points) numerical effort grows as  $O(M \log M)$ . As a function of the energy numerical effort grows as  $O(E^{3/2})$ . This is a slow rate compared to other methods. This means that for large 3D calculations this method will become more efficient.

This paper should not be concluded without putting attention on existing drawbacks in the Chebychev scheme as compared to the SOD scheme. First, the Chebychev scheme as formulated in Sec. II cannot propagate wave packets when the Hamiltonian has explicit time dependence.<sup>7,15</sup> This means that for scattering from time dependent potentials, the SOD scheme has to be used with the drawback of reduced accuracy and speed. (Expansion of the method to include periodic time dependence is in progress). Another drawback is that because of the long time durations of propagation in the Chebychev scheme intermediate results are lost.

To summarize, despite the above drawbacks the Chebychev scheme is an important step in establishing quantum mechanical time dependent methods as a routine tool in molecular dynamics. The uniform character of the Chebychev

expansion makes the scheme especially attractive when high accuracy and long propagation times are needed.

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