Efficient Numerical Solution of Time-Dependent Multichannel One-Dimensional or Radial Problems in Quantum Mechanics

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Abstract. An efficient and very accurate numerical solution of a system of coupled time-dependent Schrödinger equations with one space variable is presented. The time evolution is performed using a generalized Crank-Nicholson method whereas the space discretization is based on the finite element method and the discrete variable representation. Moreover we apply the exterior complex scaling method to avoid undesired reflections of the wave packets at the ends of the grid instead of the complex absorbing potential. Such a combination of various highly precise methods makes the resulting technique one of the most efficient for solving the system of a coupled time-dependent radial Scrödinger equations which is encountered in many problems in atomic and molecular physics.

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INTRODUCTION

In atomic, molecular, and nuclear physics many problems which are described within the quantum mechanics lead to a system of coupled time-dependent one-dimensional or radial Scrödinger equations which we write in a concise form as (for simplicity we use atomic units, i.e. we set $\hbar = 1$ and $m_e = 1$)

$$H\Psi(x,t) = i\frac{\partial\Psi(x,t)}{\partial t} \tag{1}$$

which describes a time evolution of a quantum-mechanical system whose dynamics is given by the multichannel Hamiltonian

$$H_{\alpha\beta} = \delta_{\alpha\beta}\frac{1}{2\mu}\frac{d^2}{dx^2} + V_{\alpha\beta}(x) \tag{2}$$

where μ denotes the reduced mass of the system and channel potentials $V_{\alpha\alpha}(x)$ and couplings $V_{\alpha\beta}(x)$ are responsible for the interaction within the studied system. The multichannel wave function $\Psi(x,t) = (\psi_1(x,t),\ldots,\psi_N(x,t))^T$ is usually given in the initial time $t = t_0$ in one channel $\alpha = \alpha_0$, i.e.

$$\psi_\alpha(x,t = t_0) = \delta_{\alpha\alpha_0}\psi_0(x). \tag{3}$$

Once the system (1) is solved and the wave function $\Psi(x,t)$ is known for $t > t_0$ one can extract physically relevant quantities (such as transition probabilities) from it using e.g. the Fourier transform.

Because analytical solutions are not available for most of the systems, efficient and precise numerical techniques of solving (1) are needed. The well-known and often used Crank-Nicholson method was shown not to be efficient enough for many problems and its generalization both in space discretization and time propagation were proposed by several authors (see e.g. [1, 2] and references therein). Here we propose to combine the time propagation by the use of the generalized Crank-Nicholson method with a space discretization based on the technique developed by Rescigno and McCurdy [3, 4].

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NUMERICAL METHOD

Instead of solving directly the equation (1) we will use an equivalent approach and write the wave function at the time $t+\Delta t$ in the form

$$\Psi(x,t+\Delta t) = \exp(-iH\Delta t)\Psi(x,t) \tag{4}$$

where the time-evolution operator propagates the wave function from t to $t+\Delta t$. The standard Crank-Nicholson method [1] for time propagation of the wave function can be derived from (4) if the exponential function is approximated using the diagonal Padé [1/1] rational function (see e.g. [5])

$$\exp(-iH\Delta t) \approx \frac{1-iH\Delta t/2}{1+iH\Delta t/2}. \tag{5}$$

If we use the diagonal Padé I [N/N] approximation

$$\exp(z) \approx \frac{1+a_1 z+a_2 z^2+\cdots+a_N z^N}{1-a_1 z+a_2 z^2-\cdots+(-1)^N a_N z^N} = \prod_{s=1}^{N}\left(\frac{1-z/z_s^{(N)}}{1+z/[z_s^{(N)}]^*}\right), \tag{6}$$

where $z_s^{(N)}$ are the roots of the polynomial in the numerator, we get the generalized Crank-Nicholson method [1] and the wave function at the time $t+\Delta t$ can be calculated as

$$\Psi(x,t+\Delta t) \approx \prod_{s=1}^{N} K_s^{(N)} \Psi(x,t) \tag{7}$$

where the operators $K_s^{(N)}$ are defined as

$$K_s^{(N)} = \frac{1+iH\Delta t/z_s^{(N)}}{1-iH\Delta t/[z_s^{(N)}]^*} \tag{8}$$

and $z_s^{(N)}$ are the complex roots of the numerator in the Padé I [N/N] approximation of the exponential function.

The time propagation given by (7) is more precise than the standard Crank-Nicholson method with one term (5) not only if we use the same time step Δt, but also if we use the time step greater than $N\Delta t$. Thus we obtain higher precision applying less times the operators (8) to the wave function (as it is clearly demonstrated in Table 1 for a model example).

One could even make the method faster by applying the whole product in (7) at once by precalculating the whole numerator and factorizing the whole denominator first. This would be useful if we work with full matrices. On the other hand, if the matrix representing Hamiltonian is a sparse matrix (as it is the case when using the finite element method and the DVR method, see below) then it is better to apply each operator $K_s^{(N)}$ separately, for the whole numerator or denominator in the Padé approximation (6) is not in general a sparse matrix.

To represent the Hamiltonian (2) accurately on a numerical grid (or in some basis) we implemented the finite element method (FEM) and the discrete variable representation (DVR) combined with the method of the exterior complex scaling (ECS). This method was proposed by [3, 4] as an efficient numerical grid method to solve the time-independent Schrödinger equation (its application to the time-independent multichannel radial scattering problem can be found in [6]). In references above one can found details on how to apply this method in the most efficient way.

Its application to the time-dependent Schrödinger equation was studied in [7] where it was shown that the use of the exterior complex scaling method eliminates reflections of outgoing wave packets from boundaries very efficiently. If we rotate the coordinate to the complex plane at sufficiently large distances where the interaction is negligible this method does not effect the solution on the real part of the grid which can be then used to calculate physical quantities of interest. Thus this method enables us to avoid introduction of a complex absorbing potential altogether.

Another great advantage of this method is that the local potentials and couplings $V_{\alpha\beta}(r)$ are all diagonal in the DVR basis and the kinetic energy operator matrix is band and it is represented with high accuracy owing to the use of the Gauss-Lobatto quadrature (see [3] for details). Thus this method results in very sparse matrices representing Hamiltonians (2) and operators used in the Crank-Nicholson time propagation and efficient algorithms for the matrix multiplication and inversion can be applied.

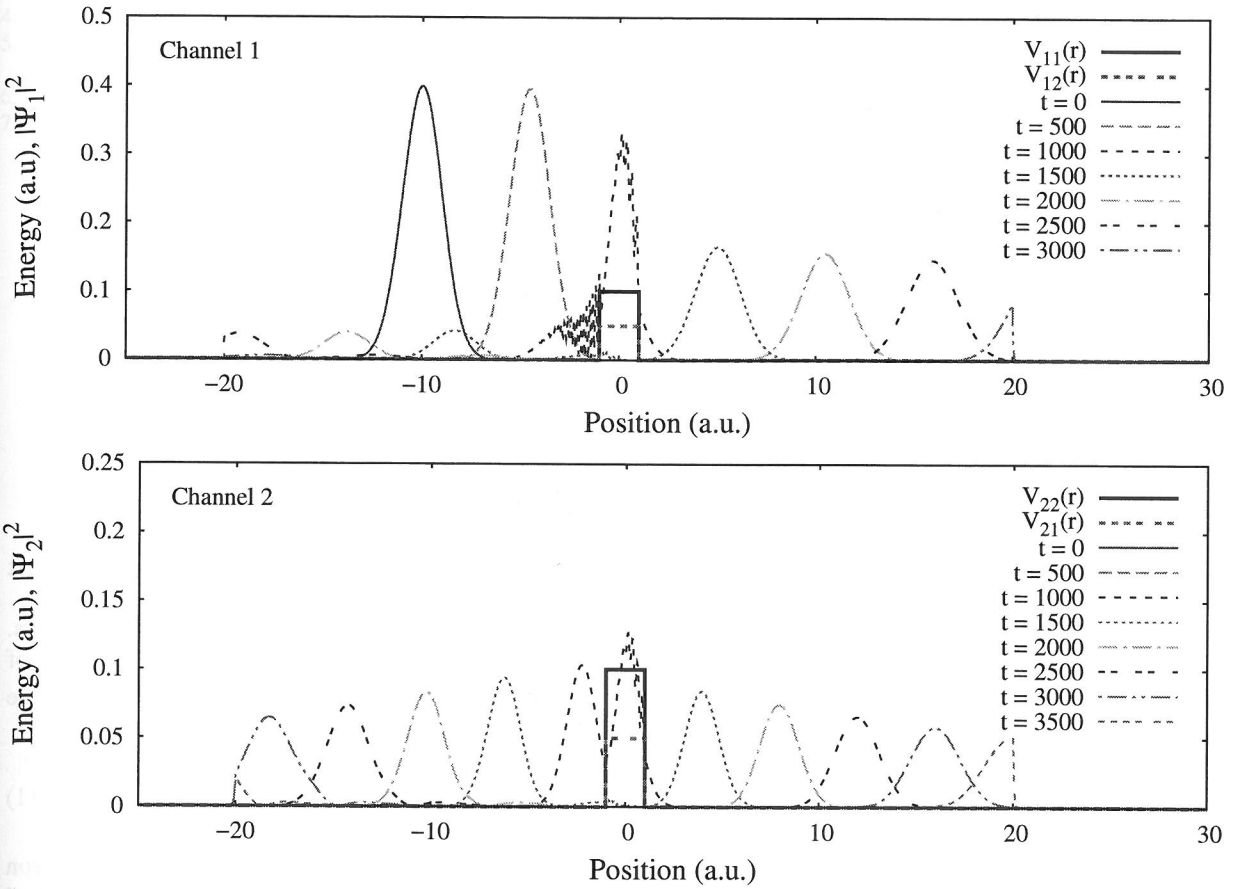

FIGURE 1. The propagation of the wave packet (10) in the two-channel barrier penetration problem (9) for $t <= 3500 a.u.$ (note that 1000 a.u. is about 24 fs), upper panel – channel 1, lower panel – channel 2. Efficient elimination of the wave packets in both channels at $x = -20$ and $x = 20$ where the complex part of the grid starts is clearly seen.

RESULTS FOR A MODEL PROBLEM

As a testing model on which the efficiency of the numerical method described above will be demonstrated has been chosen a multi-channel one-dimensional barrier penetration problem where channel potentials and couplings are potential barriers

$$V_{\alpha\beta}(x) = \delta_{\alpha\beta}\varepsilon_\alpha + \begin{cases} v_{\alpha\beta}, & |x| < a, \\ 0, & |x| > a. \end{cases} \tag{9}$$

Here we present our results for a two-channel problem with numerical values $a = 1.0$, $v_{11} = v_{22} = 0.1$, $v_{12} = v_{21} = 0.05$, $\varepsilon_1 = 0.0$, and $\varepsilon_2 = 0.05$ (all values here and below are given in atomic units).

The reduced mass μ was set to be roughly the proton mass ($\mu = 1836$) to get a time scale typical in molecular dynamics problems. The initial wave packet is non-zero only in the first channel and it has the form of the Gaussian wave packet

$$\psi_0(x) = (2\pi(\Delta x)^2)^{-1/4} \exp\left[-(x-x_0)^2/4(\Delta x)^2 + ip_0(x-x_0)\right] \tag{10}$$

with numerical values $x_0 = -10.0$, $\Delta x = 1.0$, $p_0 = 20.0$.

The basic numerical grid used in our calculations was chosen dense enough to be sure that the error in the time propagation comes mainly from the approximation of the time propagator (7). The real part of the grid was in the interval $\langle -20, 20\rangle$ and complex scaling was used for $x < -20$ and $x > 20$ with the scaling angle $\eta = 40°$.

In Fig. 1, the time propagation of the Gaussian wave packet (10) is shown for the two-channel model (9). As the wave packet arrives in the interaction region ($|x| < a$) it starts to bifurcate into both accessible channels. Due to the

TABLE 1. The number of iterations, the total number of applications of the operator $K_s^{(N)}$ on $\Psi(x,t)$, and the time step needed to get the error e_α of the wave function given by (11) for different orders of the generalized Crank-Nicholson method.

N	**iterations**	$K_s\Psi$	Δt	e_1	e_2
1	200000	200000	0.01	$1.7\ 10^{-5}$	$1.4\ 10^{-5}$
2	10000	20000	0.2	$5.6\ 10^{-8}$	$4.5\ 10^{-8}$
3	2000	6000	1.0	$3.2\ 10^{-9}$	$2.5\ 10^{-9}$
4	400	1600	5.0	$6.2\ 10^{-8}$	$5.0\ 10^{-8}$
5	200	1000	10.0	$5.1\ 10^{-8}$	$4.1\ 10^{-8}$
6	100	600	20.0	$4.5\ 10^{-7}$	$3.6\ 10^{-7}$
8	50	400	40.0	$8.9\ 10^{-7}$	$7.1\ 10^{-7}$
10	40	400	50.0	$1.7\ 10^{-8}$	$1.4\ 10^{-8}$
15	20	300	100.0	$4.4\ 10^{-9}$	$3.5\ 10^{-9}$
20	10	200	200.0	$7.9\ 10^{-6}$	$6.3\ 10^{-6}$

non-zero threshold energy ε_2 the wave packet in the second channel moves a little bit more slowly than in the first channel.

In the Table 1, we compare precision of our model calculations for several settings of time propagation parameters. The most relevant number characterizing the efficiency of a particular calculation is the number of multiplications of the wave function by the operator $K_s^{(N)}$ (the third column) through the time propagation. Quantities e_α shown in the last two columns of the table are errors of the wave functions at $t = 2000$ in both channels defined by

$$(e_\alpha)^2 = \int_{-20}^{20} dx \left|\Psi(x,t=2000) - \Psi^{exact}(x,t=2000)\right|^2 \tag{11}$$

where $\Psi^{exact}(x,t=2000)$ was taken from the very accurate propagation using the generalized Crank-Nicholson method of the order 20 and time step $\Delta t = 10.0$. We can clearly see that the generalized Crank-Nicholson method of higher orders is much superior to commonly used Crank-Nicholson method given by (5). For example, to obtain the same accuracy with the generalized Crank-Nicholson method of order 20 one needs 1000 times less matrix multiplications and back substitutions than with standard Crank-Nicholson method.

CONCLUSIONS

The efficient numerical technique which combines the finite element method, the discrete variable representation and the exterior complex scaling method for space discretization the Hamiltonian with the generalized Crank-Nicholson method for time propagation was used to solve the system of coupled one-dimensional Schrödinger equations. This method proved to be very precise and efficient and we believe that it can be successfully applied to many problems encountered in atomic and molecular physics.

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