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Exponentially fitted symplectic methods for the numerical integration of the Schrödinger equation*

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The computation of the energy eigenvalues of the one-dimensional time-independent Schrödinger equation is considered. Exponentially fitted and trigonometrically fitted symplectic integrators are obtained, by modification of the first and second order Yoshida symplectic methods. Numerical results are obtained for the one-dimensional harmonic oscillator and Morse potential.

KEY WORDS: trigonometrically fitted, exponentially fitted, Schrödinger equation, symplectic methods

AMS subject classification: 65L15

1. Introduction

The time-independent Schrödinger equation is one of the basic equations of quantum mechanics. Its solutions are required in the studies of atomic and molecular structure and spectra, molecular dynamics and quantum chemistry. In the literature many numerical methods have been developed to solve the time-independent Schrödinger equation.

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The one-dimensional time-independent Schrödinger equation may be written in the form

$$-\frac{1}{2}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V(x)\psi = E\psi, \quad x \in [a, b], \tag{1}$$

where E is the energy eigenvalue, $V(x)$ the potential, and $\psi(x)$ the wave function. Equation (1) can be rewritten in the form

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -B(x)\psi,$$

where $B(x) = 2(E - V(x))$, or

$$\begin{aligned} \phi' &= -B(x)\psi, \\ \psi' &= \phi. \end{aligned}$$

Liu et al. [2] have shown that the one-dimensional Schrödinger equation (1) has a symplectic structure. Therefore, the symplectic schemes are the reasonable numerical algorithms for solving the Schrödinger equation. In their paper [2] applied symplectic algorithms developed by Yoshida [6] in order to find the energy eigenvalues of equation (1) with boundary conditions of the type

$$y(a) = y(b) = 0.$$

In this work we develop two exponentially fitted methods based on Yoshida's first and second order symplectic methods.

2. Exponentially and trigonometrically fitted symplectic methods

Given an interval $[a, b]$ and a partition with N points

$$x_0 = a, \; x_n = x_0 + nh, \quad n = 1, 2, \ldots, N.$$

An one-step discrete scheme

$$\begin{pmatrix} \phi_{n+1} \\ \psi_{n+1} \end{pmatrix} = M_n \begin{pmatrix} \phi_n \\ \psi_n \end{pmatrix}, \quad M_n = \begin{pmatrix} \alpha_n & \beta_n \\ \gamma_n & \delta_n \end{pmatrix}$$

is symplectic if $M^T J M = J$, where

$$J = \begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}$$

2.1. *The first order method*

The first order Yoshida type method is

$$\phi_{n+1} = \phi_n - chB_n\psi_n,$$
$$\psi_{n+1} = \psi_n + dh\phi_{n+1}, \tag{2}$$

with $c = d = 1$.

We can also write this method as a two step method

$$\phi_{n+1} - 2\psi_n + \psi_{n-1} = -\beta h^2 B_n \psi_n,$$

where $\beta = c\,d$.

In order to construct the exponentially fitted method we require method (2) to integrate exactly the exponential function $\psi(x) = \mathrm{e}^{\pm wx}$ we have the following expression for β

$$\beta = \frac{\mathrm{e}^{wh} + \mathrm{e}^{-wh} - 2}{w^2h^2}.$$

For small values of w the above formula are subject to heavy cancellations. In this case the following Taylor series expansions must be used

$$\beta = 1 + \frac{v^2}{12} + \frac{v^4}{360} + \frac{v^6}{20160} + \frac{v^8}{1814400} + \frac{v^{10}}{239500800} + O(h^{12}),$$

where $v = wh$.

Similarly we obtain the trigonometrically fitted method, requiring method (2) to integrate exactly the function $\exp(\pm iwx)$, $i = \sqrt{-1}$ we have the following expression for β

$$\beta = \frac{2}{w^2h^2}(1 - \cos(wh))$$

or

$$\beta = 1 - \frac{v^2}{12} + \frac{v^4}{360} - \frac{v^6}{20160} + \frac{v^8}{1814400} - \frac{v^{10}}{239500800} + O(h^{12}).$$

It can be seen that when $w \to 0$ the above methods become the Yoshida's first order method $\beta = 1$.

2.2. *The second order method*

The two stage Yoshida type symplectic method is of the following form

$$p_1 = \phi_n - c_1 hB\psi_n,$$
$$q_1 = \psi_n + d_1 hp_1,$$
$$\phi_{n+1} = p_1 - c_2 hBq_1,$$
$$\psi_{n+1} = q_1 + d_2 h\phi_{n+1} \tag{3}$$

this method is of second order for

$$c_1 = 0, \quad c_2 = 1, \quad d_1 = d_2 = \frac{1}{2} \tag{4}$$

Requiring the method (3) to integrate exactly the exponential function $\psi(x) = e^{\pm wx}$ we have the following equations

$$\begin{aligned}
e^{wh} &= 1 + (c_1 + c_2)wh + c_2 d_1 (wh)^2 + c_1 c_2 d_1 (wh)^3, \\
e^{wh} &= 1 + d1wh + d_2 wh e^{wh} + c_1 d_1 (wh)^2, \\
e^{-wh} &= 1 - (c_1 + c_2)wh + c_2 d_1 (wh)^2 - c_1 c_2 d_1 (wh)^3, \\
e^{-wh} &= 1 - d1wh - d_2 wh e^{-wh} + c_1 d_1 (wh)^2.
\end{aligned}$$

This system is solved for c_1, c_2, d_1 and d_2 and the following coefficients are obtained for the exponentially fitted method.

$$c_1 = 0, \quad c_2 = \frac{e^{2wh} - 1}{2wh e^{wh}}, \quad d_1 = d_2 = \frac{e^{wh} - 1}{wh(e^{wh} + 1)}.$$

The following Taylor series expansions can be used in order to avoid cancellations for small w.

$$\begin{aligned}
c_2 &= 1 + \frac{v^2}{6} + \frac{v^4}{120} + \frac{v^6}{5040} + \frac{v^8}{362880} + \frac{v^{10}}{39916800} + O(h^{12}), \\
d_1 = d_2 &= \frac{1}{2} - \frac{v^2}{24} + \frac{v^4}{240} - \frac{17v^6}{40320} + \frac{31v^8}{725760} - \frac{691v^{10}}{159667200} + O(h^{12}).
\end{aligned}$$

Similarly we require method (3) to integrate exactly the function $\exp(\pm iwx)$, $i = \sqrt{-1}$ we have the following expression for the coefficients of the trigonometrically fitted method.

$$c_1 = 0, \quad c_2 = \frac{\sin(wh)}{wh}, \quad d_1 = d_2 = \frac{1}{wh} \tan\left(\frac{wh}{2}\right).$$

The following Taylor series expansions can be used in order to avoid cancellations for small w.

$$\begin{aligned}
c_2 &= 1 - \frac{v^2}{6} + \frac{v^4}{120} - \frac{v^6}{5040} + \frac{v^8}{362880} - \frac{v^{10}}{39916800} + O(h^{12}), \\
d_1 = d_2 &= \frac{1}{2} + \frac{v^2}{24} + \frac{v^4}{240} + \frac{17v^6}{40320} + \frac{31v^8}{725760} + \frac{691v^{10}}{159667200} + O(h^{12}).
\end{aligned}$$

It can be seen that when $w \to 0$ the above methods become the second order Yoshida method (4).

3. Numerical results

We consider the one-dimensional eigenvalue problem with boundary conditions

$$\psi(a) = 0, \quad \psi(b) = 0$$

We use the shooting scheme in the implementation of the above methods. The shooting method converts the boundary value problem into an initial value problem where the boundary value at the end point b is transformed into an initial value $y'(a)$, the results are independent of $y'(a)$ if $y'(a) \neq 0$. The eigenvalue E is a parameter in the computation, the value of E that makes $y(b) = 0$ is the eigenvalue computed.

3.1. The harmonic oscillator

The potential of the one dimensional harmonic oscillator is

$$V(x) = \frac{1}{2}kx^2,$$

we consider $k = 1$. The exact eigenvalues are given by

$$E_n = n + \frac{1}{2}, \quad n = 0, 1, 2, \ldots$$

In order to compute the eigenvalues by the shooting method we started with the interval $[-5.5, 5.5]$ and we increased the interval as we computed higher state eigenvalues up to $[-8.5, 8.5]$.

In the next table we compare the second order method of Liu (Meth1) and the modified trigonometrically fitted method developed here (Meth2). Results are given for steps $h = 0.1$ and $h = 0.01$. In columns 3–6 we give the absolute errors multiplied by 1000 (see also figure 1).

We see that Meth1 with step $h = 0.1$ fails to produce two correct decimal digits from E_4, for $h = 0.01$ the absolute error increase rapidly as we compute higher state eigenvalues up to 10^{-3}. Above E_{14} Meth2 with step $h = 0.1$ gives less absolute error than Meth1 with step $h = 0.01$. With step $h = 0.01$ Meth2 gives absolute errors less than 10^{-5}.

3.2. Morse potential

We now consider Morse potential

$$V(x) = D\ [\exp(-2\alpha x)\ -\ 2\exp(-\alpha x)]$$

with $D = 12$ and $\alpha = 0.204124$.

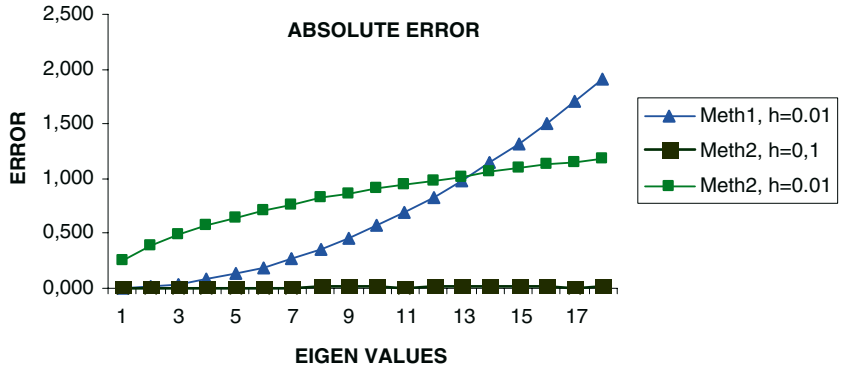

Figure 1. The harmonic oscillator.

The exact eigenvalues are given by

$$E_n = -12 + \left(n + \frac{1}{2}\right) - \frac{1}{48}\left(n + \frac{1}{2}\right)^2.$$

In order to compute the eigenvalues by the shooting method we used the interval $[-13.5, 13.5]$ up to the 11th state eigenvalue and the interval $[-13.5, 43.5]$ for higher state eigenvalues (table 1).

Table 1
The harmonic oscillator.

	Exact	Meth1 $h = 0.1$	Meth2 $h = 0.1$	Meth1 $h = 0.01$	Meth2 $h = 0.01$
E_0	0.5	0.313	0.247	0.004	0.003
E_1	1.5	1.565	0.394	0.016	0.004
E_2	2.5	4.070	0.498	0.041	0.005
E_3	3.5	7.831	0.582	0.079	0.006
E_4	4.5	12.850	0.650	0.128	0.007
E_5	5.5	19.128	0.712	0.189	0.006
E_6	6.5	26.673	0.768	0.266	0.008
E_7	7.5	35.482	0.820	0.354	0.009
E_8	8.5	45.559	0.867	0.454	0.009
E_9	9.5	56.905	0.911	0.566	0.009
E_{10}	10.5	69.522	0.945	0.688	0.006
E_{11}	11.5	83.422	0.986	0.829	0.010
E_{12}	12.5		1.021	0.979	0.011
E_{13}	13.5		1.056	1.141	0.011
E_{14}	14.5		1.091	1.316	0.011
E_{15}	15.5		1.124	1.503	0.011
E_{16}	16.5		1.151	1.699	0.007
E_{17}	17.5		1.184	1.916	0.012

In table 2 we compare the second order method of Liu (Meth1) and the modified trigonometrically fitted method developed here (Meth2). Results are given for steps $h = 0.1$ and $h = 0.01$. In columns 3–6 we give the absolute errors multiplied by 1000 (see also figure 2).

Table 2
Morse potential.

	Exact	Meth1 $h = 0.1$	Meth2 $h = 0.1$	Meth1 $h = 0.01$	Meth2 $h = 0.01$
E_0	11.505208	0.305	0.251	0.004	0.004
E_1	10.546875	1.413	0.371	0.016	0.005
E_2	9.630208	3.405	0.437	0.036	0.007
E_3	8.755208	6.056	0.478	0.063	0.008
E_4	7.921875	9.158	0.499	0.094	0.008
E_5	7.130208	12.523	0.507	0.129	0.010
E_6	6.380208	15.977	0.507	0.163	0.009
E_7	5.671875	19.362	0.498	0.197	0.009
E_8	5.005208	22.541	0.484	0.229	0.009
E_9	4.380208	25.390	0.465	0.257	0.009
E_{10}	3.796875	27.804	0.443	0.280	0.009
E_{11}	3.255208	29.694	0.448	0.298	0.008
E_{12}	2.755208	30.992	0.396	0.311	0.009
E_{13}	2.296875	31.639	0.360	0.317	0.008
E_{14}	1.880208	31.600	0.339	0.316	0.008
E_{15}	1.505208	30.856	0.295	0.308	0.008
E_{16}	1.171875	29.403	0.280	0.293	0.007
E_{17}	0.880208	27.257	0.225	0.271	0.006
E_{18}	0.630208	24.450	0.205	0.243	0.006
E_{19}	0.421875	21.031	0.156	0.208	0.005
E_{20}	0.255208	17.070	0.130	0.168	0.004

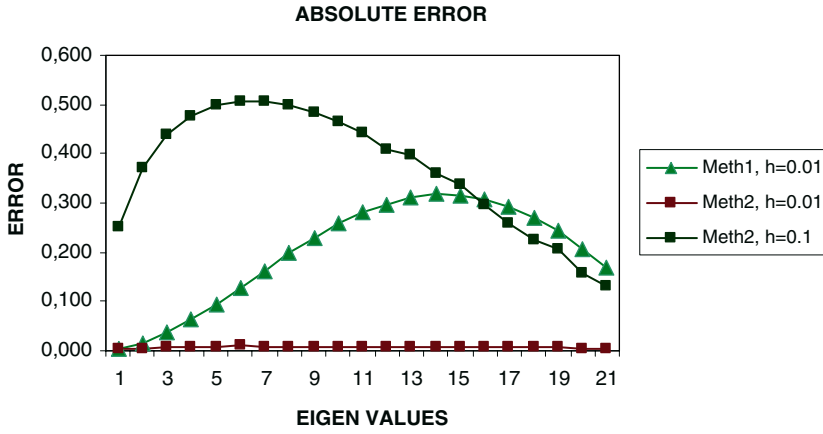

Figure 2. Morse potential.

We see that for Meth1 for both steps the errors increase rapidly as we compute higher state eigenvalues. While stable results are produced by Meth2 the absolute error does not increase further than 10^{-5} for $h = 0.01$, and 0.5×10^{-3} for $h = 0.1$. For higher state eigenvalues Meth2 with step $h = 0.1$ gives less absolute error than Meth1 with step $h = 0.01$.

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