Symplectic Schemes and the Shooting Method for Eigenvalues of the Schrödinger Equation *

LIU Xue-Shen(刘学深)**, CHI Yu-Hua(匙玉华), DING Pei-Zhu(丁培柱)
Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012

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The one-dimensional time-independent Schrödinger equation is transformed into a Hamiltonian canonical equation by means of the Legendre transformation, then the symplectic schemes and a new shooting method extended to the eigenvalues of the Schrödinger equation. The method is applied to the calculations of one-dimensional harmonic oscillator, an anharmonic oscillator and the hydrogen atom. The numerical results are in good agreement with the exact ones.

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It is well known that the time-independent Schrödinger equation is one of the basic equations of quantum mechanics and many numerical methods have been developed to solve it.[1,2] The symplectic method is the difference method that preserves the symplectic structure, and is a better method for long-time many-step calculation and for preserving the structure of the system.[3−6] Recently, the symplectic method has been used for the computation of the quantum system.[7] In our previous work,[8,9] symplectic schemes were extended to the numerical solution of the one-dimensional time-independent Schrödinger equation and two methods were developed for solving the eigenvalues and eigenfunctions. Kalogiratou *et al.*[10] presented a symplectic integrator for the numerical solution of the Schrödinger equation based on the Taylor expansion of the matrix exponential and used the shooting method to obtain the eigenvalues.

In this Letter, we present a new shooting method for eigenvalues. In the calculations, symplectic schemes are used. The method is applied to the computations of the eigenvalues of a one-dimensional harmonic oscillator, an anharmonic oscillator and the hydrogen atom. The numerical results are in good agreement with the exact ones.

The one-dimensional time-independent Schrödinger equation is expressed as (atomic units are used throughout)

$$-\frac{1}{2}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi, \tag{1}$$

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

$$\ddot{\psi} + \frac{\partial U}{\partial \psi} = 0, \tag{2}$$

where $U(x,\psi) = \frac{1}{2}B(x)\psi^2$ and $B(x) = 2[E - V(x)]$; x plays the role of the time variable, and $\psi(x)$ and $U(x,\psi)$ are regarded as a generalized coordinate and a formal potential function, respectively. Thus $\dot{\psi}(x)$ and $\ddot{\psi}(x)$ are the generalized velocity and the generalized acceleration, respectively. Equation (2) is a formal Newtonian equation and can be transformed into the following Hamiltonian canonical equation by means of Legendre transformation:[8]

$$\begin{aligned}\dot{\varphi} &= -\frac{\partial H_2(\psi,x)}{\partial \psi} = -B(x)\psi,\\ \dot{\psi} &= \frac{\partial H_1(\varphi)}{\partial \varphi} = \varphi.\end{aligned} \tag{3}$$

Its corresponding Hamiltonian function is

$$H(\varphi,\psi,x) = \frac{1}{2}\varphi^2 + \frac{1}{2}B(x)\psi^2 = H_1(\varphi) + H_2(\psi,x). \tag{4}$$

Equation (4) is a separate Hamiltonian system which includes explicitly the 'time' variable x. We can construct directly the symplectic schemes tailored to the time-dependent Hamiltonian function (4) from the known explicit symplectic schemes for excluding explicitly time by adding the assistant canonical coordinate and canonical momentum.[9,11] Thus the symplectic schemes can be extended to the solution of the time-independent Schrödinger equation.

Let the step length be h, $x_n = x_0 + nh$; the first-order symplectic scheme reads

$$\begin{aligned}\varphi^{n+1} &= \varphi^n - hB_{n+\frac{1}{2}}\psi^n,\\ \psi^{n+1} &= \psi^n + h\varphi^{n+1},\end{aligned} \tag{5}$$

where $B_{n+\frac{1}{2}} = B\left(x_n + \frac{1}{2}h\right) = 2\left[E - V\left(x_n + \frac{1}{2}h\right)\right]$.

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** Email: yashuliu@email.jlu.edu.cn

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Eliminating φ^n and φ^{n+1} in Eq. (5) yields

$$\psi^{n+1} - \left[2 - h^2 B_{n+\frac{1}{2}}\right]\psi^n + \psi^{n-1} = 0, \qquad (6)$$

which is a tridiagonal symmetric matrix eigenvalue equation. Equation (6) is a three-layer scheme and can be written as

$$\psi^{n+1} = \left[2 - h^2 B_{n+\frac{1}{2}}\right]\psi^n - \psi^{n-1}.$$

The two-stage second-order symplectic scheme reads

$$\begin{aligned}
&p^1 = \varphi^n, \quad q^1 = \psi^n + (1/2)hp^1,\\
&x_{n_1} = x_n + (1/2)h;\\
&\varphi^{n+1} = p^1 - hB(x_{n_1})v_1, \quad \psi^{n+1} = q^1 + (1/2)h\varphi^{n+1},\\
&x_{n+1} = x_{n_1} + (1/2)h = x_n + h; \qquad (7)
\end{aligned}$$

which can be written as

$$\begin{pmatrix}\varphi^{n+1}\\ \psi^{n+1}\end{pmatrix} = \begin{pmatrix} 1-\frac{1}{2}h^2 B_{n+\frac{1}{2}} & -hB_{n+\frac{1}{2}} \\ h-\frac{1}{4}h^3 B_{n+\frac{1}{2}} & 1-\frac{1}{2}h^2 B_{n+\frac{1}{2}}\end{pmatrix}\begin{pmatrix}\varphi^n\\ \psi^n\end{pmatrix}.$$

With the same procedure as stated above, we obtain

$$\left(1 - \frac{1}{4}h^2 B_{n-\frac{1}{2}}\right)\psi^{n+1} - \left[2 - \frac{3}{4}h^2\left(B_{n+\frac{1}{2}} + B_{n-\frac{1}{2}}\right)\right]\psi^n + \left(1 - \frac{1}{4}h^2 B_{n+\frac{1}{2}}\right)\psi^{n-1} = 0, \qquad (8)$$

which is a generalized matrix eigenvalue equation.

The four-stage fourth-order symplectic scheme reads

$$\begin{aligned}
&p^1 = \varphi^n - hc_0 B(x_n)\psi^n, \quad q^1 = \psi^n + hd_1 p^1,\\
&x_{n_1} = x_n + hd_1;\\
&p^2 = p^1 - hc_1 B(x_{n_1})q^1, \quad q^2 = q^1 + hd_2 p^2,\\
&x_{n_2} = x_{n_1} + hd_2;\\
&p^3 = p^2 - hc_2 B(x_{n_2})q^2, \quad q^3 = q^2 + hd_3 p^3,\\
&x_{n_3} = x_{n_2} + hd_3;\\
&\varphi^{n+1} = p^3 - hc_3 B(x_{n_3})q^3, \quad \psi^{n+1} = q^3 + hd_4\varphi^{n+1},\\
&x_{n+1} = x_{n_3} + hd_4 = x_n + h; \qquad (9)
\end{aligned}$$

where

$$\begin{aligned}
&c_0 = 0,\ c_1 = c_3 = \alpha,\ c_2 = \beta,\\
&d_1 = d_4 = \alpha/2,\ d_2 = d_3 = (\alpha+\beta)/2,
\end{aligned}$$

or

$$\begin{aligned}
&c_0 = c_3 = \alpha/2,\ c_1 = c_2 = (\alpha+\beta)/2,\\
&d_1 = d_3 = \alpha,\ d_2 = \beta,\ d_4 = 0.
\end{aligned}$$

and $\alpha = (2 - 2^{1/3})^{-1}$, $\beta = 1 - 2\alpha$.

Denoting $a_i^n = -c_i B(x_{n_i})$, $i = 0, 1, 2, 3$, $b_i = d_i$, $i = 1, 2, 3, 4$, Eq. (9) becomes

$$\begin{aligned}
&p^1 = \varphi^n + ha_0\psi^n, \quad q^1 = \psi^n + hb_1 p^1,\\
&p^2 = p^1 + ha_1 q^1, \quad q^2 = q^1 + hb_2 p^2,\\
&p^3 = p^2 + ha_2 q^2, \quad q^3 = q^2 + hb_3 p^3,\\
&\varphi^{n+1} = p^3 + ha_3 q^3, \quad \psi^{n+1} = q^3 + hb_4\varphi^{n+1}, \qquad (10)
\end{aligned}$$

Here we have denoted $a_i = a_i^n$, $x_n = x_{n_0}$ for convenience. Equation (10) can be written in the matrix form

$$\begin{aligned}
\begin{pmatrix}\varphi^{n+1}\\ \psi^{n+1}\end{pmatrix} &= \begin{pmatrix}1 & a_3 h\\ b_4 h & 1 + a_3 b_4 h^2\end{pmatrix}\begin{pmatrix}1 & a_2 h\\ b_3 h & 1 + a_2 b_3 h^2\end{pmatrix}\\
&\cdot\begin{pmatrix}1 & a_1 h\\ b_2 h & 1 + a_1 b_2 h^2\end{pmatrix}\begin{pmatrix}1 & a_0 h\\ b_1 h & 1 + a_0 b_1 h^2\end{pmatrix}\\
&\cdot\begin{pmatrix}\varphi^n\\ \psi^n\end{pmatrix}\\
&= \begin{pmatrix}M_{11}^n & M_{12}^n\\ M_{21}^n & M_{22}^n\end{pmatrix}\begin{pmatrix}\varphi^n\\ \psi^n\end{pmatrix},
\end{aligned}$$

where

$$\begin{aligned}
M_{11}^n =& 1 + [a_1 b_1 + a_2(b_1 + b_2) + a_3(b_1 + b_2 + b_3)]h^2\\
&+ [a_1 b_1 a_3 b_3 + a_1 b_1 b_2(a_2 + a_3)\\
&+ a_2 a_3 b_3(b_1 + b_2)]h^4 + a_1 b_1 a_2 b_2 a_3 b_3 h^6,\\
M_{12}^n =& (a_0 + a_1 + a_2 + a_3)h\\
&+ [a_0 a_1 b_1 + a_3 b_3(a_0 + a_1 + a_2)\\
&+ (a_2 + a_3)(a_0 b_2 + a_0 b_1 + a_1 b_2)]h^3\\
&+ [a_0 a_1 b_1 a_3 b_3 + a_0 a_1 b_1 b_2(a_2 + a_3)\\
&+ a_2 a_3 b_3(a_0 b_2 + a_0 b_1 + a_1 b_2)]h^5\\
&+ a_0 a_1 b_1 a_2 b_2 a_3 b_3 h^7,\\
M_{21}^n =& (b_1 + b_2 + b_3 + b_3)h\\
&+ [a_3 b_3 b_4 + a_1 b_1(b_2 + b_3 + b_4)\\
&+ (b_1 + b_2)(a_2 b_4 + a_2 b_3 + a_3 b_4)]h^3\\
&+ [a_1 b_1 a_3 b_3 b_4 + a_2 a_3 b_3 b_4(b_1 + b_2)\\
&+ a_1 b_1 b_2(a_2 b_4 + a_2 b_3 + a_3 b_4)]h^5\\
&+ a_1 b_1 a_2 b_2 a_3 b_3 b_4 h^7,\\
M_{22}^n =& 1 + [a_0 b_1 + (a_0 + a_1)(b_2 + b_3 + b_4)\\
&+ a_2 b_3 + (a_2 + a_3)b_4]h^2\\
&+ [a_0 a_1 b_1(b_3 + b_4) + a_3 b_3 b_4(a_0 + a_1)\\
&+ a_2 a_3 b_3 b_4 + a_0 a_1 b_1 b_2 + (a_2 b_4 + a_2 b_3 + a_3 b_4)\\
&\cdot(a_0 b_2 + a_0 b_1 + a_1 b_2)]h^4\\
&+ [a_0 a_1 b_1 a_3 b_3 b_4 + a_2 a_3 b_3 b_4(a_0 b_2 + a_0 b_1\\
&+ a_1 b_2) + a_0 a_1 b_1 b_2(a_2 b_4 + a_2 b_3 + a_3 b_4)]h^6\\
&+ a_0 a_1 b_1 a_2 b_2 a_3 b_3 b_4 h^8.
\end{aligned}$$

With the same procedure stated above, we have

$$M_{21}^{n-1}\psi^{n+1} - (M_{21}^{n-1} M_{22}^n + M_{21}^n M_{11}^{n-1})\psi^n$$

$$+ M_{21}^{n}(M_{11}^{n-1}M_{22}^{n-1} - M_{21}^{n-1}M_{12}^{n-1})\psi^{n-1} = 0, \tag{11}$$

which is a generalized matrix eigenvalue equation. Equation (11) has the following form:

$$C_1\psi^{n+1} - C_2\psi^{n} + C_3\psi^{n-1} = 0,$$

and

$$\psi^{n+1} = C_1^{-1}(C_2\psi^{n} - C_3\psi^{n-1}), \tag{12}$$

which is a three-layer scheme, where C_1, C_2, C_3 are the coefficients of Eq. (11).

Now we consider the one-dimensional eigenvalue problem under the boundary conditions

$$\psi(a) = 0, \quad \psi(b) = 0. \tag{13}$$

In order to obtain the eigenvalues, we can solve the tridiagonal symmetric matrix eigenvalue equation (6), which is a first-order symplectic scheme. For high-order symplectic schemes, for example the second-order scheme (8) or the fourth-order scheme (11), it is very difficult to solve the matrix eigenvalue problem with the generalized matrix eigenvalue equation. A new shooting method for eigenvalues is presented as follows.

Equations (8) and (11) can be solved easily if the values of ψ^0 and ψ^1 are known. The boundary conditions (13) can be written as $\psi^0 = \psi(a) = 0$ and $\psi^N = \psi(b) = 0$. Letting $\psi^1 = \text{const} \neq 0$, we can yield the solutions $(\psi^0, \psi^1, \psi^2, \psi^3, \cdots, \psi^N)$ by using the symplectic scheme (8) or (13). In the calculation, we take $\psi^1 = 1$. The solutions are independent of ψ^1 for $\psi^1 \neq 0$ due to $\psi^0 = 0$, thus we may find the value of parameter E that makes $\psi^N = 0$. The coefficients C_1, C_2, C_3 are a function of parameter E. According to the right boundary condition, the parameter E that makes $\psi^N = 0$ is the eigenvalue that we need to compute, and the corresponding $\psi^0, \psi^1, \psi^2, \psi^3, \cdots, \psi^N$ are the eigenfunctions.

We apply the new shooting method and the symplectic scheme to the calculations of the eigenvalues of one-dimensional harmonic oscillator, anharmonic oscillator and the hydrogen atom.

The potential of the one-dimensional harmonic oscillator is taken to be

$$V(x) = \frac{1}{2}x^2, \quad (-\infty < x < +\infty). \tag{14}$$

The exact eigenvalues of the harmonic oscillator are given by

$$E_n = n + \frac{1}{2}, \quad (n = 0, 1, 2, \cdots). \tag{15}$$

The eigenvalues obtained from the fourth-order symplectic scheme by using the new shooting method are listed in Table 1 together with the exact ones. It is shown that the numerical results are in good agreement with the exact ones, even for the larger excitation number of the level.

Table 1. Eigenvalues of the one-dimensional harmonic oscillator together with the exact ones. Here n is the excitation number of the level, E_s is the present results (space step $h = 2 \times 10^{-4}$).

n	Exact	E_s	n	Exact	E_s
	$(a = -10, b = 10)$			$(a = -20, b = 20)$	
0	0.50	0.50000000011	40	40.50	40.50000000017
1	1.50	1.50000000015	41	41.50	41.50000000017
2	2.50	2.50000000015	42	42.50	42.50000000019
3	3.50	3.50000000015	43	43.50	43.50000000018
4	4.50	4.50000000011	44	44.50	44.50000000018
21	21.50	21.50000000017	45	45.50	45.50000000018
22	22.50	22.50000000014	46	46.50	46.50000000020
23	23.50	23.50000000016	47	47.50	47.50000000020
24	24.50	24.50000000017	48	48.50	48.50000000017
25	25.50	25.50000000018	49	49.50	49.50000000019

The potential of anharmonic oscillators is taken to be

$$V(x) = \frac{1}{2}x^2 + \lambda x^{2\alpha}, \quad (-\infty < x < +\infty). \tag{16}$$

The energy eigenvalues of the quartic anharmonic oscillator characterized by the potential (16) for $\lambda = 1/2$, $\alpha = 2$ with the new shooting method and the fourth-order symplectic scheme are listed in Table 2 together with the results of Banerjee *et al.*,[12] who obtained the results from the non-perturbative method by using an appropriately scaled basis for the expansion of each eigenfunction. Table 2 shows that energy eigenvalues of quartic anharmonic oscillator with the new shooting method are in good agreement with the results of Banerjee *et al.*

Table 2. Energy eigenvalues of the quartic anharmonic oscillator ($a = -10$, $b = 10$, space step $h = 10^{-4}$). Here n is the excitation number of the level, E_s is the results of this work, E_B is the results of Banerjee *et al.*[12]

n	E_s	E_B
0	0.69617582283417	0.69617582076514
1	2.32440635249079	2.32440635210604
2	4.32752497918173	4.32752497887965
3	6.57840194975984	6.57840194902495
4	9.02877871917746	9.02877871815164
5	11.6487207262958	11.6487207256116
10	26.7245510704608	26.7245510698326
20	63.8088888983235	63.8088888976775
30	107.389841775172	107.389841774588
40	155.915759135701	155.915759134850
50	208.528131643387	208.528131642424
100	517.772091573445	517.772091569455

The radial wavefunction of hydrogen atom is determined by the Schrödinger equation in the form

$$\ddot{\psi}(r) + \left[2E + \frac{2}{r} - \frac{l(l+1)}{r^2}\right]\psi(r) = 0, \quad (0 \leq r < +\infty) \tag{17}$$

where $l = 0, 1, 2, \cdots$ and $\psi(r)$ is the radial wavefunction. For the bound states, the boundary conditions are

$$\psi(0) = 0, \quad \psi(+\infty) = 0. \tag{18}$$

The exact eigenvalues are calculated by the formula

$$E_n = -\frac{1}{2n^2}, \quad (n = 1, 2, 3, \cdots). \tag{19}$$

We also solve the eigenvalues by using the fourth-order symplectic scheme and the new shooting method for $l = 0$. The numerical results are present in Table 3 along with the exact values. It can be seen again that the eigenvalues for the hydrogen atom converge to the exact values.

Table 3. Eigenvalues of the hydrogen atom ($a = 0$, space step $h = 10^{-4}$).

	Exact	E_s
E_1	-0.5000000	-0.4999999989 ($b = 17$)
E_2	-0.1250000	-0.1249999991 ($b = 47$)
E_3	-0.0555556	-0.0555555172 ($b = 47$)

In summary, the symplectic schemes have been extended to the numerical solution of one-dimensional time-independent Schrödinger equation and a new shooting method is presented. The new shooting method and the symplectic schemes are applied to the calculations of the eigenvalues of one-dimensional harmonic oscillator, anharmonic oscillator and the hydrogen atom. The numerical results illustrate that the eigenvalues of this work converge to the exact ones and have a high accuracy. The values of φ do not need to be calculated and the high-order symplectic schemes can be used easily with the new shooting method. Thus we need less computer time with the new shooting method compared to the SSSM presented in Ref. [8].

References

[1] Cooney P J, Kanter E P and Vager Z 1981 *Am. J. Phys.* **49** 76

[2] Ley-Koo E, Mateos-Cortes S and Villa-Torres G 1995 *Int. J. Quant. Chem.* **56** 175

[3] Feng K, Wu H M and Qin M Z 1990 *J. Comput. Math.* **8** 371

[4] Hong J L and Liu Y 2003 *Appl. Math. Lett.* **16** 759

[5] Liu X S and Ding P Z 2004 *Chin. Phys. Lett.* **21** 230

[6] Li Y J 2003 *Chin. Phys. Lett.* **20** 486

[7] Ding P Z, Wu C X, Mu Y K et al 1996 *Chin. Phys. Lett.* **13** 245

[8] Liu X S, Liu X Y et al. 2000 *Int. J. Quantum Chem.* **79** 343

[9] Liu X S, Su L W and Ding P Z 2002 *Int. J. Quantum Chem.* **87** 1

[10] Kalogiratou Z, Monovasilis Th and Simos T E 2003 *J. Comput. Appl. Math.* **158** 83

[11] Sanz-Serna J M and Portillo A 1996 *J. Chem. Phys.* **104** 2349

[12] Banerjee K, Bhatnagar S P, Choudhry V and Kanwal S S 1978 *Proc. R. Soc. London* A **360** 575