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ON THE NUMERICAL SOLUTION OF THE SCHRÖDINGER EQUATION IN ONE DIMENSION [1]

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A simple and accurate method for solving the time-independent one-dimensional Schrödinger equation is proposed. The procedure is based on a Taylor expansion of the propagation matrix for the eigenfunctions, which allows one improve accuracy systematically. As the algorithm only requires one-step calculations, it is suitable for small personal computers. Results are shown for anharmonic oscillators which are customarily used as models to study the vibration spectra of diatomic molecules. The effect of using approximate finite boundary conditions is discussed.

I. INTRODUCTION

It is nowadays possible to solve the time-independent Schrödinger equation in one-dimension, numerically with the desired degree of accuracy. However, there has lately been an increasing interest in algorithms that are suitable for microcomputer calculations [1] (and references therein). Most of such procedures are based on replacing the second derivative $D^2 (D = \mathrm{d}/\mathrm{d}x)$ by the operator

$$\delta_h^2 = h^{-2}(e^{hD} + e^{-hD} - 2), \tag{1}$$

which can be expanded as

$$\delta_h^2 = D^2 + 2\sum_{j=2}^{\infty} \frac{h^{2j-2}}{(2j)!} D^{2j}. \tag{2}$$

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When D^2 is replaced by δ_h^2 in the eigenvalue equation

$$\psi''(x) = q(x)\psi(x), \quad q(x) = V(x) - E, \tag{3}$$

a three-term recurrence relation is obtained with an error of $O(h^2)$ [1]. The accuracy is improved by choosing a set of numbers $c_1, c_2, ..., c_n$ so that

$$\sum_{j=1}^{n} c_j \delta_{jh}^2 = D^2 + O(h^{2n}). \tag{4}$$

Even more accurate algorithms are developed by means of the linear operator

$$L = \sum_{j=-k}^{k} (a_j e^{jhD} - h^2 b_j D^2 e^{jhD}), \tag{5}$$

in which the numbers a_j and b_j are determined so that $L(f_i) = 0$ for a properly chosen set of functions $\{f_1, f_2, ...\}$ [2]. The price one has to pay to increase accuracy in these ways is that the eigenvalue equation becomes a multi-step algorithm which demands more computation time and memory space and is not so easily tractable by means of small personal computers.

Killingbeck [3] proposed a simpler alternative method that consists of replacing D^4 by $q(x)^2$ in Eq. (2). This substitution is justified by first-order perturbation theory and leads to a two-step algorithm with an error of only $O(h^4)$.

In this paper we present a simple and highly accurate one-step integration procedure based on the propagation matrix [3-5]. It is wellknown that the wavefunction $\psi(x)$ and its first derivative $\psi'(x)$ propagate according to

$$\Phi(x+h) = T(x+h, x)\Phi(x), \tag{6}$$

where

$$\Phi(x) = \begin{pmatrix} \psi(x) \\ \psi'(x) \end{pmatrix}, \tag{7}$$

and $T(x+h, x)$ is the 2×2 propagator matrix, which for our purposes is most conveniently written

$$T(x+h, x) = \begin{pmatrix} u(x,h) & v(x,h) \\ \frac{\partial u(x,h)}{\partial h} & \frac{\partial v(x,h)}{\partial h} \end{pmatrix}. \tag{8}$$

Here the functions u and v are two linearly independent solutions of the differential equation

$$\frac{\partial^2 w(x,h)}{\partial h^2} = q(x+h)w(x,h), \tag{9}$$

with the initial conditions

$$u(x,0) = \frac{\partial v(x,h)}{\partial h}|_{h=0} = 1, \qquad v(x,0) = \frac{\partial u(x,h)}{\partial h}|_{h=0} = 0. \tag{10}$$

Let us assume for the moment that acceptable approximations to $u(x,h)$ and $v(x,h)$ are available for all x values. The solutions to the differential equation (3) can be propagated forward from 0 to $x_R > 0$ and backward from 0 to $x_L < 0$ according to

$$T(x_R, 0) = T(x_R, x_R - h) \ldots T(2h, h)T(h, 0), \tag{11a}$$

$$T(x_L, 0) = T(x_L, x_L + h) \ldots T(-2h, -h)T(-h, 0), \tag{11b}$$

respectively. Therefore, boundary conditions at x_L and x_R are easily expressed in terms of the matrix elements of $T(x_R, 0)$ and $T(x_L, 0)$. For instance, if

$$\psi(x_R) = \psi(x_L) = 0$$

we have from Eq. (8) that

$$u(x_R, 0)v(x_L, 0) - v(x_R, 0)u(x_L, 0) = 0. \tag{12}$$

The problem is greatly simplified when the potential $V(x)$ is parity invariant and $x_L = -x_R$ because in this case the solutions of the eigenvalue equation have definite parity so that $\psi'(x = 0) = 0$ or $\psi(x = 0) = 0$ when they are even or odd, respectively. As a result it is sufficient to propagate the solutions in the forward direction and the eigenvalues are given by the roots of $u(x_R, 0)v(x_R, 0) = 0$.

In order to treat problems with boundary conditions at infinity one chooses sufficiently large values of $-x_L$ and x_R so that the change of the results is smaller than a prescribed tolerance when the interval $x_R - x_L$ is increased. The effect of the approximate finite boundary conditions is diminished by using the correct asymptotic form of the wavefunction. The logarithmic derivative $f(x) = -\psi'(x)/\psi(x)$ satisfies the Riccati equation $f'(x) - f(x)^2 + q(x) = 0$. An approximate solution of the latter equation for large x values is $f(x) \approx q(x)^{1/2} + q'(x)/[4q(x)]$. Therefore, more accurate results are expected if the Dirichlet boundary conditions $\psi(x) = 0$ at $x = x_L$ and $x = x_R$ are replaced by

$$\psi'(x) = -\{q(x)^{1/2} + q'(x)/[4q(x)]\}\psi(x). \tag{13}$$

The algorithm developed here is particularly suitable for this improvement because the wavefunction and its first derivative are treated on equal footing. The functions $u(x,h)$ and $v(x,h)$ can be approximated in many different ways. One may use, for example, perturbation theory [3,4] or power series expansions [5]. Because in our opinion the latter possibility is simpler and has not been fully exploited, we discuss it here.

If $\psi(x)$ analytic at x, we can write

$$\psi(x+h) = \sum_{j=0}^{\infty} \psi_j(x) h^j, \tag{14}$$

where the Taylor coefficients $\psi_j(x)$ can be obtained by successive differentiation of the Schrödinger equation. All such coefficients are linear combinations of $\psi(x)$ and $\psi'(x)$, and contain derivatives of $q(x)$. In ref. [5] $q(x)$ was approximated by a linear function of x, so that the derivatives of order greater than one vanish. Besides, part of the series for $\psi(x)$ and $\psi'(x)$ in (14) was exactly summed obtaining a propagator which is exact for a constant potential and accurate to order h^{10} for a linear potential. Here we expect to obtain more accurate results by simply adding higher derivatives of the potential function. In this way the potential function is more adequately described within each interval $(x, x+h)$ allowing the use of a larger step size h without loss of of accuracy. More precisely, if $q(x)$ is analytic at x, we write

$$q(x+h) = \sum_{j=0}^{\infty} q_j(x) h^j, \qquad w(x,h) = \sum_{j=0}^{\infty} w_j(x) h^j, \tag{15}$$

which when substituted into Eq. (9) lead to the following expression for the coefficients w_j

$$w_{j+2}(x) = \frac{1}{(j+1)(j+2)} \sum_{i=0}^{j} q_i(x) w_{j-i}(x), \tag{16}$$

The starting point is $w_o(x) = 1$, $w_1(x) = 0$ for $w(x,h) = u(x,h)$ and $w_o(x) = 0$, $w_1(x) = 1$ for $w(x,h) = v(x,h)$. In principle, all the Taylor coefficients for $u(x,h)$ and $v(x,h)$ can be obtained from the recurrence relation (16). In practice, the procedure may be hindered by the difficulty of obtaining the derivatives of the potential function. If such derivatives became exceedingly complex, one may truncate the Taylor series for $q(x)$, thus obtaining a polynomial approximation to this function. This alternative may be considered as a generalization of the algorithm proposed in Ref. [5].

When $V(x)$ is a polynomial function of the coordinate of degree k, the sum in (16) has at most $k+1$ terms for all j values and highly accurate calculations are easily carried out. As an example we consider the Schrödinger equation with the quartic potential energy function

$$V(x) = x^4, \tag{17}$$

because several of its eigenvalues have been calculated with high accuracy. In this case Eq. (8) becomes

$$w_{j+2} = \frac{1}{(j+1)(j+2)}((x^4 - E)w_j + 4x^3 w_{j-1} + 6x^2 w_{j-2} + 4x w_{j-3} + w_{j-4}), \tag{18}$$

where $w_j = 0$ if $j < 0$.

The lowest eigenvalues of the quartic anharmonic oscillator obtained with several truncated Taylor expansion for u and v and several h values are shown in Table

Table 1

First four eigenvalues of $H = -D^2 + x^4$, obtained from the Dirichlet boundary condition at $x_R = 4.0$. The largest power of h in u and v is indicated as $O(h^N)$ and n represents the quantum number.

h	$O(h^4)$	$O(h^8)$	$O(h^{12})$
		$n = 0$	
0.4.	1.06122697341927817	1.06036087646177527	1.06036209343705561
0.2	1.06046171163192288	1.06036209042108940	1.06036209048462957
0.1	1.06036938061217416	1.06036209049228853	1.06036209048418297
Ref. [8,9]			1.060362090484183
		$n = 1$	
0.4	3.82460742531559007	3.79966566654150645	3.79967302649491913
0.2	3.80131424886906183	3.79967304391438127	3.79967302980195977
0.1	3.79977261392056136	3.79967302993426146	3.79967302980139440
Ref. [8,9]			3.799673029801394
		$n = 2$	
0.4	7.57838911202742850	7.45573942180112915	7.45569789287405183
0.2	7.46425163590578971	7.45569829754300541	7.45569793798670719
0.1	7.45621971522852105	7.45569793963541250	7.45569793798670719
Ref. [8,9]			7.455697937986738
		$n = 3$	
0.4	11.99399574067826170	11.64516659822164310	11.64474531948848920
0.2	11.67235509917848440	11.64474817643553790	11.64474551139882860
0.1	11.64647905485898650	11.64474552229038950	11.64474551137817480
Ref. [8,9]			11.64474551137816

1. Since the potential is parity invariant, the boundary conditions $\psi(\pm\infty) = 0$ are replaced by either $\psi'(0) = 0$, $\psi(\infty) = 0$ or $\psi(0) = 0$, $\psi(\infty) = 0$ for even or odd states, respectively, in which a sufficiently large value of x_R is substituted for ∞. In the present case $x_R = 4$ is found to be large enough. As the eigenvalues are completely determined by the boundary conditions at $x = 0$ and $x = x_R$, only the propagation in the forward direction is necessary.

For comparison purposes we have also calculated the eigenvalues of the quartic oscillator by means of the kth-order constant (reference potential) perturbative method CPM(k) [3,4] and results are shown in Table 2 for k=0, 1 and 2. We conclude that our method requires only about 35% of the computation time and 30% of the memory space necessary for a CPM calculation with the same accuracy.

Similar results are obtained when the Dirichlet boundary condition $\psi(x_R) = 0$ is replaced by the Von Neuman one $\psi'(x_R) = 0$ at the same x_R value. If the calculation is sufficiently accurate, the approximate eigenvalue obtained from the Dirichlet (Von Neumann) boundary condition tends to the actual eigenvalue from

Table 2

First four eigenvalues of $H = -D^2 + x^4$, obtained from the Dirichlet boundary condition at $x_R = 4.0$. The functions u and v are approximated by the $CPM(k)$ [3, 4].

h	$CPM(0)$	$CPM(1)$	$CPM(2)$
		$n = 0$	
0.8			1.0598026886
0.4	1.1188113605	1.0631559077	1.0603596266
0.2	1.0748756724	1.0606567325	1.0603620817
0.1	1.0603946266	1.0603645407	
Ref. [8,9]			1.060362090484183
		$n = 1$	
0.8			3.0598026886
0.4	3.9427630178	3.8094078810	3.7996607669
0.2	3.8356673157	3.8005266246	3.7996729923
0.1	3.7995970386	3.7996978208	
Ref. [8,9]			3.799673029801394
		$n = 2$	
0.8			7.4482258488
0.4	7.6517990135	7.4755773731	7.4556631952
0.2	7.5053067384	7.4572997653	7.4556978969
0.1	7.4681346978	7.4558303636	
Ref. [8,9]			7.455697937986738
		$n = 3$	
0.8			11.6348262310
0.4	11.8876390312	11.6786173725	11.6446718214
0.2	11.7066890007	11.6476572592	11.6447459048
0.1	11.6603061559	11.6449592827	
Ref. [8,9]			11.64474551137816

Table 3

Lowest eigenvalue of $H = -D^2 + x^4$ obtained from the Dirichlet boundary condition (DBC) and from Eq. (13) for $x_R = 2.0$.

h	DBC	Eq. (13)
0.4	1.07328268	1.060053103
0.2	1.07264948	1.059586301
0.1	1.07262096	1.059573711

above (below) as $x_R \to \infty$ [6]. In order to compare the accuracy of the eigenvalues obtained from the Dirichlet boundary condition with those obtained from the roots of Eq. (13) for $x = x_R$, we repeated the calculation using smaller values of x_R.

Table 4

First four eigenvalues of $H = -D^2/2 + x^2/2 + \alpha x^3 + \beta x^4$ for $\alpha = 0.005$ and $\beta = 0.005$, obtained from the Dirichlet boundary conditions at $x_L = -7.0$ and $x_R = 7.0$.

h	$O(h^4)$	$O(h^8)$	$O(h^{12})$
		$n = 0$	
0.100	0.503656976697375890	0.503654915173656331	0.503654915171875287
0.050	0.503656976697375890	0.503654915171880418	0.503654915171875286
0.025	0.503654921914727716	0.503654915171875303	0.503654915171875286
Ref. [10]			0.5036549151718752
		$n = 1$	
0.100	1.51808024773427004	1.51806640970786452	1.51806640969215377
0.050	1.51806720724052245	1.51806640969220357	1.51806640969215377
0.025	1.51806645728286209	1.51806640969215394	1.51806640969215377
Ref. [10]			1.518066409692154
		$n = 2$	
0.100	2.54652107867966299	2.54647212619802626	2.54647212611600319
0.050	2.54647499995448817	2.54647212611627455	2.54647212611600314
0.025	2.54647229922082066	2.54647212611600410	2.54647212611600314
Ref. [10]			2.546472126116003
		$n = 3$	
0.100	3.58850015401629503	3.58837651000681252	3.58837650970413842
0.050	3.58838386534358451	3.58837650970517065	3.58837650970413820
0.025	3.58837695552888970	3.58837650970414191	3.58837650970413820
Ref. [10]			3.588376509704138

Results for $x_R = 2$ are shown in Table 3. We conclude that a given accuracy is attained with smaller x_R values when the boundary condition (13) is used instead of the Dirichlet one. The practical importance of this substitution is that it results in a smaller computation time, which is most valuable when using a slow computer.

We next consider $V(x) = x^2/2 + \alpha x^3 + \beta x^4$ as an example of an asymmetric potential. For the sake of simplicity the potential parameters are chosen so that there is just one well (i.e. $\alpha^2 < 16\beta/9$). The most convenient starting point for the propagation is the minimum (say x_m) of $V(x)$. The two unknowns, namely, E and $\psi'(x_m)/\psi(x_m)$ are obtained from the boundary conditions $\psi(x_L) = \psi(x_R) = 0$. Results are shown in Table 4 for $\alpha = 0.005$ and $\beta = 0.005$.

The algorithm discussed above is suitable for studying the vibrational-rotational spectra of diatomic molecules. As an example we consider here the Morse potential energy function

$$V(r) = D\{exp[-2a(r - r_e)] - 2exp[-a(r - r_e)]\}, \qquad (19)$$

where r_e is the equilibrium distance and D and a are potential parameters. Here we choose $D = 188.4355$, $r_e = 1.9985$ and $a = 0.711248$, which apply to the

Table 5

First four eigenvalues of the Morse oscillator with potential energy,

$$V(r) = D\{exp[-2a(r-r_e)] - 2exp[-a(r-r_e)]\},$$

where $D = 188.4355$, $r_e = 1.9985$ and $a = 0.711248$, obtained from the Dirichlet boundary conditions at $x_L = -1.8$ and $x_R = 6.0$, $x = r - r_e$.

h	$O(h^4)$	$O(h^8)$	$O(h^{12})$
		$n = 0$	
0.100	-178.793526507544789	-178.798537820233933	-178.798538351020784
0.050	-178.798286537449280	-178.798538349647613	-178.798538351031350
0.025	-178.798524851268348	-178.798538351027456	-178.798538351031351
exact			-178.798538351031350
		$n = 1$	
0.100	-160.257502423032333	-160.283422153501176	-160.283425629204350
0.050	-160.282019924643610	-160.283425619304765	-160.283425629350030
0.025	-160.283346936078766	-160.283425629319587	-160.283425629350054
exact			-160.283425629350051
		$n = 2$	
0.100	-142.707406011717610	-142.780046978285688	-142.780060341879918
0.050	-142.775900084054265	-142.780060301654344	-142.780060342676620
0.025	-142.779821131726809	-142.780060342547273	-142.780060342676757
exact			-142.780060342676752
		$n = 3$	
0.100	-126.142330665749831	-126.288406925011714	-126.288442488415472
0.050	-126.279658355677974	-126.288442374844842	-126.288442491010986
0.025	-126.287926796327781	-126.288442490631708	-126.288442491011459
exact			-126.288442491011453

hydrogen molecule. The lowest purely vibrational energy levels obtained by means of the Dirichlet boundary conditions at $x_L = -1.8$ and $x_R = 6.0$, $x = r - r_e$, are shown in Table 5. The agreement with exact results is remarkable.

The algorithm presented here is suitable for small computers because it is based on a one-step procedure which requires little memory space. In addition to this, the procedure is remarkably simple and treats the wavefunction and its first derivative on the same level. The latter fact makes it possible to implement improved boundary conditions that take into account the asymptotic behaviour of the wavefunction. The accuracy of the results can be systematically improved provided that the potential function be at least piecewise continuous in (x_L, x_R) and can be adequately approximated by a polynomial in each interval $(x, x+h)$. A Taylor expansion of the potential function in every interval proves to be the simplest strategy provided the derivatives can be obtained, otherwise one may try a polynomial interpolation instead. If h is small enough one does not expect a

noticeable loss of accuracy when the latter approximation is used.

One-dimensional "supersingular" potentials of the form $V(x) = x^2 + \lambda x^\nu$ ($\nu < -2$, $\lambda > 0$), $0 < x < \infty$ [7] can be treated as asymmetric potentials. The boundary conditions in this case are $\psi(0) = \psi(\infty) = 0$.

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