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An accurate method for numerical calculations in quantum mechanics

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Abstract

An accurate method for numerical calculations of matrix elements and for solving the eigenvalue problem in quantum mechanics is presented. Methods for numerical interpolation, differentiation and integration provide 15-digit accuracy with double-precision arithmetic operations. A method for solution of the eigenvalue problem of an ordinary differential equation by using discretization and matrix eigenvalue methods provides 13- to 15-digit accuracy. The efficiency of the proposed methods is demonstrated by the applications to bound states for the linear harmonic oscillator, anharmonic oscillators, the Morse potential and the modified Pöschl–Teller potential.

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1. Introduction

Since the development of wave mechanics [1] the Schrödinger equation has been applied to many fields in quantum mechanics [2–6]. Exact analytic solutions with special or other mathematical functions are obtained for limited cases of, for example, a free particle, linear harmonic oscillator and hydrogen atom. Approximation methods for solutions, such as perturbation, variation and Wentzel–Kramers–Brillouin (WKB), have been extensively used but their applicable range is rather restricted for practical problems. In order to overcome these limitations, numerical methods of solution by matching or shooting wavefunctions obtained by the Numerov method have been developed for atomic structure calculations since the early days of wave mechanics [7–11]. Though pioneering works have provided fruitful insight into atomic structure calculations, errors in numerical calculations are usually larger than 1.0D-8 ($= 1.0 \times 10^{-8}$) for eigenvalues, so that further improvements in accuracy are necessary. The approach via shooting for eigenvalues and expectation values, and using Richardson extrapolation for eigenvalues, has been proposed in [12–20] but provides no description of the accuracy of the eigenfunctions, off-diagonal matrix elements between

different eigenfunctions or matrix elements such as derivatives. Another method of solution is the discretized matrix eigenvalue problem [21–25]. Though the higher-order finite difference formulae for the second derivative have been used, the eigenvalues had only 8-digit accuracy. Accurate calculation of eigenvalues and eigenfunctions, and of matrix elements, is basic to a wide range of applications of quantum mechanics.

The main theme of the present paper is highly accurate calculations for quantum mechanics using the simplest possible methods. They are very useful in large-scale computations in atomic and molecular physics. Our final aim is to calculate matrix elements such as total energies, transition probabilities in photoabsorption and photoelectron spectra of atoms and molecules; high accuracy is required for the case where small matrix elements play an important role, for example, inelastic collisions between charged particles and molecules. In previous papers [26, 27] we presented a method of accurate single-centre and multicentre numerical integration and demonstrated its applicability to atomic structure and molecular orbital calculations, respectively. Matrix elements for atomic structure calculations with 15-digit accuracy, which is the highest accuracy achieved in double-precision arithmetic operations, were obtained by using Gaussian quadrature rules for the exact analytic solution of a hydrogenic basis function. Matrix elements with 10-digit accuracy were obtained for the numerical basis set, in which the wavefunction is given in a tabular form at discrete points, and functions at other points are calculated by interpolation. The topics needing improvement for these investigations are the accuracy relating to the integrand, because a loss of significant digits occurs frequently during a process involving a large number of computations. The first topic for improvement is interpolation with 10-digit accuracy because it is used ubiquitously. The second topic is numerical derivatives. The calculation of derivatives has been generally avoided because adequate accuracy has not been achieved. This, however, restricts the applicability of the numerical calculations. The third topic is numerical integration. In addition to Gaussian quadrature rules, accurate numerical integration using functions only at tabular points is frequently used during the process of calculation. The fourth topic is improvement in the accuracy of eigenvalues and eigenfunctions of the Schrödinger equation. Although a large number of references on numerical analysis [28–37], interpolation [38–40], numerical derivatives [28, 29, 31, 41, 42], integration [42–47], the two-point boundary-value problem of ordinary differential equations [48–50] and the eigenvalue problem of the Schrödinger equation [12–25] show formulae and typical examples of calculations, the ultimate performance of the calculation method has not yet been fully investigated. It is a challenging and non-trivial problem to overcome the loss of accuracy in these arithmetic operations. After trials for improving accuracy we found that the classical methods, such as Lagrange interpolation, numerical derivatives, central-difference integration formula and finite difference methods, provide accurate results. Though they are well known, their ultimate performance has not been well recognized. Since the classical methods are simple, they serve as powerful tools across a wide range of research areas. Since the problem is general, we summarize the relation between quantum mechanics and numerical calculations in section 2. In section 3 we present the calculation method. Section 4 is devoted to results and discussion. We take examples from the one-dimensional potential problem, the linear harmonic oscillator [1–6,51], anharmonic oscillators of the potential $v(\xi) = \mu\xi^2 + \lambda\xi^4$ [12, 14, 15, 18, 19, 23, 24, 52–70] and $V(\xi) = \xi^2 + \lambda\xi^2/(1 + g\xi^2)$ [18, 23, 24, 71–79], the Morse potential [2–6, 19, 22, 25, 51, 80–84] and the modified Pöschl–Teller potential [3–5] in order to clearly demonstrate the performance of our method, as accurate solutions by other techniques exist in many fields of physics and chemistry. Applications to atomic structure calculations will be published elsewhere. In the appendix, the central-difference integration formula of high degree is derived.

2. Relation between quantum mechanics and numerical calculation

The one-electron Hamiltonian of quantum mechanics in one dimension is given by

$$H = -(\hbar^2/2m)(\mathrm{d}/\mathrm{d}x)^2 + U(x) \tag{1}$$

where the first term is a kinetic energy with mass m and Dirac constant $\hbar$ and the second term is the potential energy. The wavefunction ψ_ν belonging to the eigenenergy E_ν of the quantum number $\boldsymbol{\nu}$ satisfies the Schrödinger equation

$$H\psi_\nu = E_\nu\psi_\nu \tag{2}$$

with suitable boundary conditions. Thus the eigenvalue problem in quantum mechanics is the boundary-value problem of the second-order ordinary differential equation.

With the wavefunctions we can calculate matrix elements of the operator $A = A(x, \mathrm{d}/\mathrm{d}x, (\mathrm{d}/\mathrm{d}x)^2)$:

$$\langle\nu|A|\nu'\rangle = \int_{-\infty}^{\infty} \mathrm{d}x\ \psi_\nu(x)A\psi_{\nu'}(x). \tag{3}$$

The matrix elements are, for example, the orthonormal integral $\langle\nu|\nu'\rangle = \delta_{\nu\nu'}$ for the operator $A = 1$, position $\langle\nu|x|\nu'\rangle$, momentum $\langle\nu| - \mathrm{i}\hbar(\mathrm{d}/\mathrm{d}x)|\nu'\rangle$, potential energy $\langle\nu|U(x)|\nu'\rangle$ and kinetic energy $\langle\nu| - (\hbar^2/2m)(\mathrm{d}/\mathrm{d}x)^2|\nu'\rangle$. The orthonormal integral with analytic exact wavefunctions provides a check on the accuracy of numerical integration and on the accuracy of the integrand calculated using the interpolation. The matrix elements of the position and potential energy also give another check on numerical integration. The matrix elements of the momentum and kinetic energy give a check on the first and second derivatives calculated by using numerical differentiation. The relation between the eigenvalue and expectation value of the Hamiltonian also gives another check on the accuracy of the matrix elements:

$$E_\nu = \langle\nu|H|\nu\rangle/\langle\nu|\nu\rangle = \langle\nu| - (\hbar^2/2m)(\mathrm{d}/\mathrm{d}x)^2 + U(x)|\nu\rangle/\langle\nu|\nu\rangle. \tag{4}$$

In evaluating the matrix elements it is important to accurately calculate integrals and integrands at the tabular points and at the intermediate points between the tabular points. In the following, we proceed to calculate accurate interpolation, numerical derivatives, numerical integration and to solve the eigenvalue problem of ordinary differential equations.

3. Numerical methods of calculation

3.1. Interpolation

Let the mesh points for x be taken equidistant along the linear scale x and a function $y = f(x)$ be given in a tabular form at these discrete points. Let us take a function $y = f(x)$ at $(n + 1)$ points $y_k = f(x_k)$, $k = 0, 1, 2, \ldots, n$, where x_k is arranged in increasing order, and let us calculate the function $f(x)$ at an intermediate point by interpolating between these points. Since the interpolation is used ubiquitously in numerical calculations, it should be simple and accurate. Though methods of interpolation have long been known, their accuracy has not been carefully studied. We demonstrate here that a method of interpolation satisfying the above requirements is the classical Lagrangian interpolation [28, 29, 33, 38–40], where the function is approximated by a polynomial $p_n(f, x)$ of degree n:

$$f(x) = p_n(f, x) + R_n \tag{5}$$

where

$$p_n(f, x) = \sum_{k=0}^{n} \ell_k(x) f(x_k) \tag{6}$$

and the polynomials $\ell_k(x)$ of degree n are the Lagrangian interpolation coefficients:

$$\ell_k(x) = \prod_{j=0,\, j\neq k}^{n} (x - x_j)/(x_k - x_j). \tag{7}$$

The remainder term R_n is given by

$$R_n = \pi_n(x) f[x_0, x_1, \ldots, x_n, x] \approx \pi_n(x) f^{(n+1)}(\xi)/(n+1)! \tag{8}$$

$$\pi_n(x) = \prod_{i=0}^{n} (x - x_i), \tag{9}$$

where $f[x_0, x_1, \ldots, x_n, x]$ denotes the divided difference [28, 38–40] and $f^{(n+1)}(\xi)$ is the $(n+1)$th derivative at $x_0 \leqslant \xi \leqslant x_n$. In the case of equidistant intervals, that is, $h = (x_n - x_0)/n$, the truncation error depends on h, n and $f^{(n+1)}(\xi)$. If the function $f(x)$ is continuous and smooth, the truncation error is reduced by increasing n, with a suitable choice of h determined by numerical experiments as described later, though the use of lower-order interpolation polynomials has often been recommended [37]. The classical method with Lagrangian interpolation polynomials is also useful if there are many interpolated functions at the same point because the Lagrangian interpolation coefficient at that point is calculated only once and can be used repeatedly. This is often the case in physical problems. The accurate interpolation enables us to calculate numerical derivatives and integrals by using higher-order interpolation polynomials.

3.2. Numerical derivative

The numerical derivative at any point can be calculated in two steps. First, the derivatives at the tabulated points are calculated by using the derivative formula obtained by differentiating the Lagrangian interpolation formula (6) and evaluating the derivatives at the tabular points. For the equidistant interval h, the mth derivative of $y = f(x)$ at $x_k, k = 0, 1, \ldots, n$, is given in the form

$$[(\mathrm{d}/\mathrm{d}x)^m y]_k = (m!/h^m)\left[(1/n!)\sum_{j=0}^{n} {}_{mn}A_{kj}\, y_j + {}_{mn}E_k\right] \tag{10}$$

where the coefficients ${}_{mn}A_{ki}$ and the truncation errors ${}_{mn}E_k$ up to $n = 10$ are tabulated in [29, 41]. The formula at the central point is mainly used because the truncation error is minimum. We obtain the formula at the centre x_i of the $(n+1)$ points for $n = 12$ given by

$$\begin{aligned}[(\mathrm{d}/\mathrm{d}x)^2 y]_i = (1/h^2)(1/831\,600)[&-50y_{i-6} + 864y_{i-5} - 7425y_{i-4} + 44\,000y_{i-3} \\ &- 222\,750y_{i-2} + 1425\,600y_{i-1} - 2480\,478y_i \\ &+ 1425\,600y_{i+1} - 222\,750y_{i+2} + 44\,000y_{i+3} \\ &- 7425y_{i+4} + 864y_{i+5} - 50y_{i+6}] + \mathrm{O}(h^{14})\end{aligned} \tag{11}$$

and for $n = 14$

$$\begin{aligned}[(\mathrm{d}/\mathrm{d}x)^2 y]_i = (1/h^2)(1/75\,675\,600)[&900y_{i-7} - 17\,150y_{i-6} + 160\,524y_{i-5} \\ &- 1003\,275y_{i-4} + 4904\,900y_{i-3} - 22\,072\,050y_{i-2} + 132\,432\,300y_{i-1} \\ &- 228\,812\,298y_i + 132\,432\,300y_{i+1} - 22\,072\,050y_{i+2} + 4904\,900y_{i+3} \\ &- 1003\,275y_{i+4} + 160\,524y_{i+5} - 17\,150y_{i+6} + 900y_{i+7}] + \mathrm{O}(h^{16}).\end{aligned} \tag{12}$$

The formulae at the non-central point are exceptionally used at points near the edge of the whole interval, where the central point formula cannot be used. We can calculate the second derivative

either by using the expression for $m = 2$ in equation (10) or by using the first derivative twice; both methods are useful. The derivatives can be calculated accurately by choosing the degree n and the width of the interval h as described later. Second, the derivatives at points other than tabulated ones are obtained by interpolating between derivatives at tabular points using the Lagrangian interpolation method as described earlier. Since the Lagrangian interpolation is accurate, errors in the derivatives come from those at the tabular points.

In evaluating the derivatives, the error of the numerical derivative consists of the truncation error $(m!/h^m)_{mn}E_k$ and the round-off error [29, 34, 37]. The truncation error of the first derivative at the tabular point is given in the form $c_{n,1}h^n f^{(n+1)}(\xi)$ and that of the second derivative at the central point is $c_{n,2}h^n f^{(n+2)}(\xi)$, where $c_{n,1}$ and $c_{n,2}$ are coefficients that are decreasing functions of n. The round-off errors for the first and second derivatives are proportional to $1/h$ and $1/h^2$, respectively.

3.3. Numerical integration

Accurate numerical integration by evaluating functions only at the tabular points can be achieved by using the central-difference integration formula [28]. Let us take a function $y = f(x)$ at discrete and distinct $(n + 1)$ points $y_k = f(x_k)$, centred at x_i, $k = i - (n/2)$, $i-(n/2)+1, \ldots, i-1, i, i+1, \ldots, i+(n/2)$, where n is an even number and x_k is arranged in increasing order. The integration formula over the three central points with interval $[x_{i-1}, x_{i+1}]$ is given in the form

$$\int_{x_{i-1}}^{x_{i+1}} f(x)\,\mathrm{d}x = h[B_{i-(n/2)}f_{i-(n/2)} + B_{i-(n/2)+1}f_{i-(n/2)+1} + \cdots + B_{i-1}f_{i-1} + B_i f_i + B_{i+1}f_{i+1} + \cdots + B_{i+(n/2)-1}f_{i+(n/2)-1} + B_{i+(n/2)}f_{i+(n/2)}] + \mathrm{O}(h^{n+2}) \tag{13}$$

where B_k are constants. Here, in addition to the functions within the interval, the functions outside the interval are also used for evaluating the integral [39]. The integration formulae for $n = 2$ (Simpson's rule) and 4 have been shown in [9]. We obtain new integration formulae, with small truncation errors, for $n = 6$ and 8 given, respectively, by

$$\int_{x_{i-1}}^{x_{i+1}} f(x)\,\mathrm{d}x = (h/3780)[5f_{i-3} - 72f_{i-2} + 1503f_{i-1} + 4688f_i + 1503f_{i+1} - 72f_{i+2} + 5f_{i+3}] + \mathrm{O}(h^9) \tag{14}$$

and

$$\int_{x_{i-1}}^{x_{i+1}} f(x)\,\mathrm{d}x = (h/113\,400)[-23f_{i-4} + 334f_{i-3} - 2804f_{i-2} + 46\,378f_{i-1} + 139\,030f_i + 46\,378f_{i+1} - 2804f_{i+2} + 334f_{i+3} - 23f_{i+4}] + \mathrm{O}(h^{11}). \tag{15}$$

The numerical integration over the whole interval can be performed by repeated use of these formulae.

Another accurate method of numerical integration over the whole interval $(-\infty, \infty)$ with a small number of integration points is the Gauss–Hermite quadrature rule:

$$\int_{-\infty}^{\infty} f(x)\,\mathrm{d}x = \int_{-\infty}^{\infty} \exp(-x^2)F(x)\,\mathrm{d}x = \sum_{k=1}^{n} \omega_k F(x_k) \tag{16}$$

where

$$F(x) = f(x)\exp(x^2) \tag{17}$$

and where x_k are zeros of the Hermite polynomials $H_n(x)$ of degree n and ω_k is a weight of the Gauss–Hermite quadrature rule [42–47]:

$$H_n(x) = (-1)^n \exp(x^2)(\mathrm{d}/\mathrm{d}x)^n \exp(-x^2) = 2xH_{n-1}(x) - 2(n-1)H_{n-2}(x) \tag{18}$$

$$\omega_k = 2^{n+1} n! \pi^{1/2} / [H_{n+1}(x_k)]^2. \tag{19}$$

The function at x_k values that are usually different from the tabular points can be calculated by using the accurate interpolation formula in section 3.1.

3.4. Numerical solution of the eigenvalue problem of ordinary differential equations by using the matrix eigenvalue method

The differential equation can be transformed into the matrix eigenvalue problem by applying discretization in space coordinates. By using the formula for a second-order derivative at the centre x_i of the $(n+1)$-discretized points:

$$[(\mathrm{d}/\mathrm{d}x)^2 y]_i = a_n y_{i+(n/2)} + a_{n-1} y_{i+(n/2)-1} + \cdots + a_{(n/2)+1} y_i + \cdots + a_0 y_{i-(n/2)} \tag{20}$$

where $a_k = (2/h^2)(1/n!)_{2,n} A_{(n/2),k}$, the differential equation is written as a matrix eigenvalue equation:

$$AY = EY \tag{21}$$

where

$$A = \begin{pmatrix}
a_{(n/2)} + U_0 & a_{(n/2)-1} & \cdots & a_0 & 0 & 0 & \cdots & & & \cdots \\
a_{(n/2)+1} & a_{(n/2)} + U_1 & a_{(n/2)-1} & \cdots & a_0 & 0 & \cdots & \cdots & & \cdots \\
a_{(n/2)+2} & a_{(n/2)+1} & a_{(n/2)} + U_2 & a_{(n/2)-1} & \cdots & a_0 & 0 & \cdots & & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & 0 & \cdots & \cdots \\
a_n & a_{n-1} & \cdots & a_{(n/2)+1} & a_{(n/2)} + U_{(n/2)} & a_{(n/2)-1} & \cdots & a_0 & 0 & \cdots \\
0 & a_n & a_{n-1} & \cdots & a_{(n/2)+1} & a_{(n/2)} + U_{(n/2)+1} & a_{(n/2)-1} & \cdots & a_0 & 0 & \cdots \\
0 & 0 & a_n & a_{n-1} & \cdots & a_{(n/2)+1} & a_{(n/2)} + U_{(n/2)+2} & \cdots & \cdots & a_0 & \cdots \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots
\end{pmatrix} \tag{22}$$

$$E = \begin{pmatrix}
E_0 & 0 & 0 & \cdots & 0 \\
0 & E_1 & 0 & \cdots & 0 \\
0 & 0 & E_2 & \cdots & 0 \\
\cdots & \cdots & \cdots & \cdots & \cdots \\
0 & 0 & 0 & \cdots & E_N
\end{pmatrix} \tag{23}$$

and

$$Y = (y_0, y_1, y_2, y_3, \ldots, y_N)^t \tag{24}$$

where $(N+1)$ is the total number of discretized points and a superscript t denotes the transpose of a vector. Though there are $(N+1)$ eigenvalues and eigenfunctions, only a small number of states that have physical meaning are required. We have to appropriately choose the whole interval in order to avoid deterioration in the accuracy of the eigenvalues and eigenfunctions. The whole interval should be selected so that the magnitude of the tail of the eigenfunction at both ends is small enough, but not too small, in order to avoid deterioration due to numerical errors. From our numerical experiment, the whole interval is adjusted so that the magnitude of the tail of the normalized eigenfunction with the maximum quantum number that is required by the problem ranges over 1.0D-15 to 1.0D-10 at both ends of the whole interval in order to get the relative errors of the eigenvalues around 1.0D-15. Though the formula of the lowest order for the second derivative, $[(\mathrm{d}/\mathrm{d}x)^2 y]_i = (y_{i+1} - 2y_i + y_{i-1})/h^2$, has been extensively used [48–50], its accuracy is not good enough. By using a high degree formula for the second derivative and choosing the appropriate whole interval, we obtain accurate eigenvalues and eigenfunctions as shown later, though the accuracy was not good enough in [23–25]. The necessary matrix

eigenvalue solvers have been provided by many authors [35–37]. The eigenvalue is calculated by using the Householder transformation for matrix tridiagonalization and the bisection method based on Sturm's theorem [35,36]. The eigenvector is calculated by using an inverse iteration method [35, 36] and normalized by using the accurate central-difference integration formula in section 3.3.

Equation (4) may be regarded as a self-consistent equation for E_ν because the eigenfunction is calculated by using the eigenvalue. Now we can calculate the matrix elements on the right-hand side by using the accurate numerical differentiation and integration described in the preceding subsections. Both the eigenvalues and matrix elements converge to their exact values by increasing the degree n of the second derivative. Numerical experience indicates that the matrix elements converge faster than the eigenvalues, as will be shown later. Coincidence of the two computed quantities provides a method of cross-checking the accuracy between them.

In concluding this section we note the relative and absolute errors. We show the relative error or accurate digits for eigenvalues and integrals such as matrix elements. We show absolute errors for integrands such as normalized wavefunctions and their derivatives, since absolute-error control is important for such integrands for practical numerical integration.

4. Results and discussion

4.1. Linear harmonic oscillator

As a typical application of the new calculation method, we take the linear harmonic oscillator, because the analytic properties of its solution are well known. The potential is $U(x) = \frac{1}{2}m\omega^2x^2$, where ω is the angular frequency [1–6]. The potential is symmetric with respect to $x = 0$ and infinite as $|x| \to \infty$. The number of bound states is infinite for this potential. The Schrödinger equation can be reduced to dimensionless form by introducing units of energy $E_0 = \frac{1}{2}\hbar\omega$ and of length $\xi = \alpha x$, $\alpha = (\hbar/m\omega)^{1/2}$ and $\lambda = E/E_0$, so that it can be rewritten as

$$(-\mathrm{d}^2/\mathrm{d}\xi^2 + \xi^2)\psi = \lambda\psi. \tag{25}$$

The solution with quantum number ν is given by the Hermite polynomial $H_\nu(\xi)$:

$$\lambda_\nu = 2\nu + 1, \qquad \nu = 0, 1, 2, \ldots \tag{26}$$

$$\psi_\nu(\xi) = (\alpha/\pi^{1/2}2^\nu\nu!)^{1/2}\exp[-\tfrac{1}{2}\xi^2]H_\nu(\xi). \tag{27}$$

The discrete mesh points along the ξ axis are allocated with equidistant width h. The wavefunctions are tabulated at these points.

Figure 1(a) shows the magnitude of the absolute errors of the wavefunctions for $\nu = 0$–7 in the interval [0, 10], evaluated at the centres of the interval $h = \frac{1}{64}$ by using the Lagrange interpolation. The absolute errors of interpolation with degree 9 are less than 1.0D-15 and the interpolation often gives exact values shown by nearly vertical lines. Interpolation with degree 3 has absolute errors of less than 1.0D-7. The errors as a function of ξ and ν can be understood in terms of the derivative $f^{(n+1)}(\xi)$ in equation (8). Applying the well-known recurrence relation $(\mathrm{d}/\mathrm{d}\xi)\psi_\nu(\xi) = (\nu/2)^{1/2}\psi_{\nu-1}(\xi) - [(\nu+1)/2]^{1/2}\psi_{\nu+1}(\xi)$ n times, we see that $(\mathrm{d}/\mathrm{d}\xi)^{n+1}\psi_\nu(\xi)$ is given by a product of $\exp[-\frac{1}{2}\xi^2]$ and a sum of the Hermite polynomials with maximum degree $\xi^{\nu+n+1}$ of $H_{\nu+n+1}(\xi)$. The asymptotic form of the error at large ξ is determined by $\exp[-\frac{1}{2}\xi^2]$ and the error increases for large ν because of the polynomial with maximum degree $\xi^{\nu+n+1}$. Figure 1(b) shows the absolute error as a function of degree for $\xi = 0.492\,1875$ with $\nu = 0$ for $h = \frac{1}{64}$, $\frac{1}{32}$, $\frac{1}{16}$ and $\frac{1}{8}$. With increasing degree, the error decreases for all ξ and ν, rapidly for smaller h, and is below 1.0D-15 for degree 9 at $h = \frac{1}{64}$

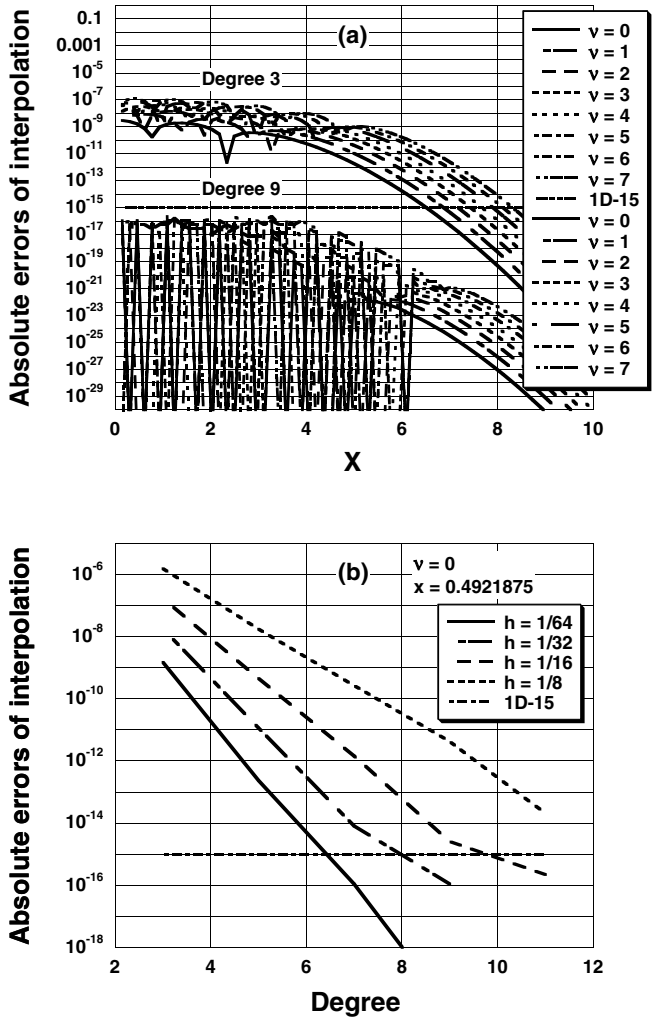

Figure 1. Absolute errors of interpolation for (a) wavefunctions with quantum numbers $\nu = 0$–7 at centres of the interval h using Lagrange interpolation of degree 3 and degree 9, and for (b) wavefunctions with $\nu = 0$ as a function of the degree of Lagrange interpolation for $h = \frac{1}{64}, \frac{1}{32}, \frac{1}{16}$ and $\frac{1}{8}$. Absolute values are taken for the errors.

and $\frac{1}{32}$. The errors as a function of n and h can be understood in terms of $\pi_n(\xi)/(n+1)!$ in equation (8); they are decreasing functions of n with a factor h^n. These results show that the polynomial interpolation provides simple and accurate evaluation of functions for most practical purposes.

Figure 2(a) shows absolute errors in the first derivative of the wavefunctions for $\nu = 0$–7, numerically evaluated at the mesh points for the interval $h = \frac{1}{64}$. The absolute errors in the first derivative with degree 10 are less than 1.0D-14 and the first derivative also gives exact values shown by nearly vertical lines. The first derivative with degree 4 has absolute errors of less than 1.0D-6. The errors as a function of ξ and ν can be understood in terms of the $f^{(n+1)}(\xi)$ of the truncation error $c_{n,1}h^n f^{(n+1)}(\xi)$. Figure 2(b) shows the absolute error as a function of the degree for $\xi = 0.5$ with $\nu = 1$ for $h = \frac{1}{64}, \frac{1}{32}, \frac{1}{16}$ and $\frac{1}{8}$. The error decreases with increasing degree for smaller h. The flattening of the error for small $h = \frac{1}{64}$ at n larger

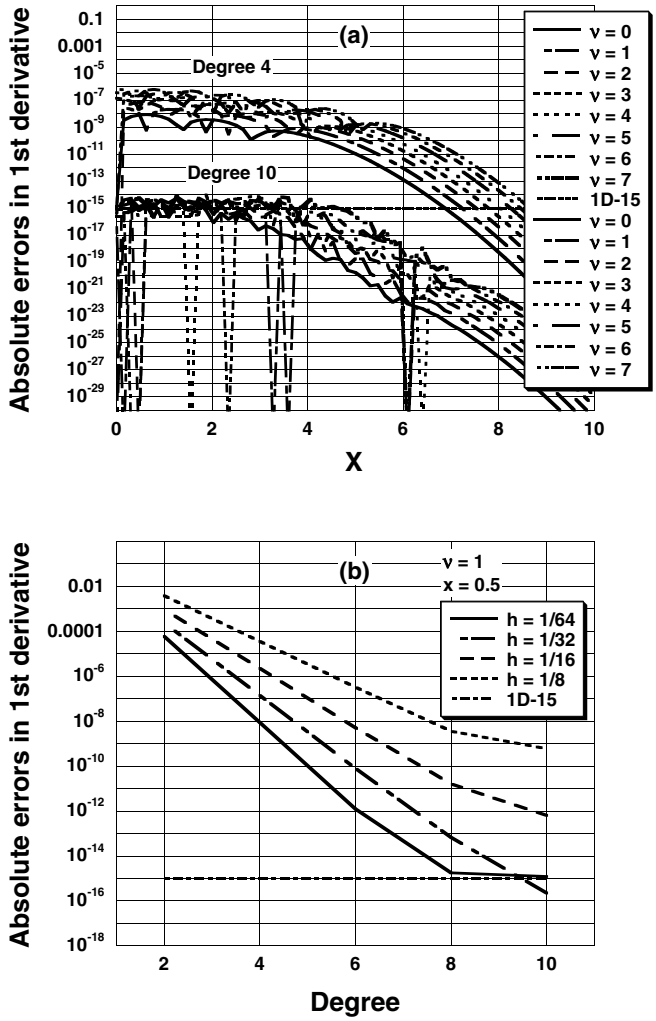

Figure 2. Absolute errors in numerical first derivative of (a) wavefunctions for quantum numbers $\nu = 0$–7 at mesh points with the interval h using first derivative formulae of degree 4 and degree 10, and of (b) wavefunctions with $\nu = 1$ as a function of the degree of first derivative formulae for $h = \frac{1}{64}, \frac{1}{32}, \frac{1}{16}$ and $\frac{1}{8}$. Absolute values are taken for the errors.

than 8 is due to the round-off error proportional to $1/h$ for the first derivative. These results show that the numerical first derivative provides accurate evaluation of the derivatives for most practical purposes.

Figure 3(a) shows absolute errors in the second derivative of the wavefunctions for $\nu = 0$–7, numerically evaluated at the mesh points for the interval $h = \frac{1}{64}$ using equation (10) with $m = 2$. The absolute errors in the second derivative with degree 10 are less than 1.0D-12 and those with degree 4 are less than 1.0D-6. The errors as a function of ξ and ν can also be understood in terms of the truncation error $c_{n,2}h^n f^{(n+2)}(\xi)$. Figure 3(b) shows the absolute error as a function of the degree for $\xi = 0.5$ with $\nu = 1$ for $h = \frac{1}{64}, \frac{1}{32}, \frac{1}{16}$ and $\frac{1}{8}$ evaluated by using equations (10)–(12) with $m = 2$. For the two larger values of h ($h = \frac{1}{8}$ and $\frac{1}{16}$), the error decreases monotonically or becomes constant with increasing degree. However, for the two

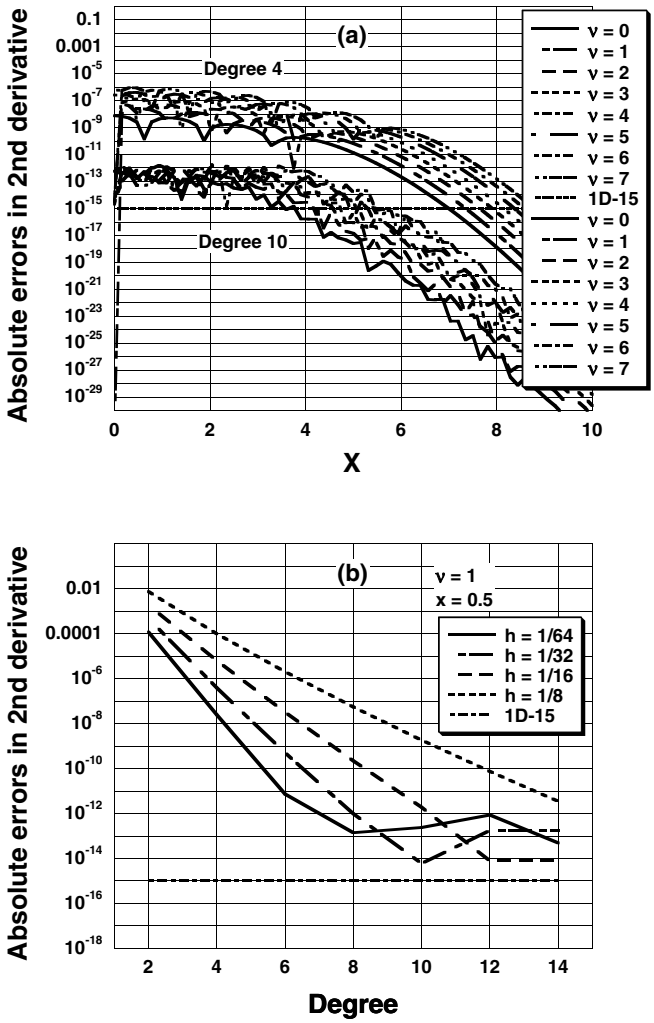

Figure 3. Absolute errors in numerical second derivative of (a) wavefunctions for quantum numbers $\nu = 0$–7 at mesh points with the interval h using second derivative formulae of degree 4 and degree 10, and of (b) wavefunctions with $\nu = 1$ as a function of the degree of second derivative formulae for $h = \frac{1}{64}, \frac{1}{32}, \frac{1}{16}$ and $\frac{1}{8}$. Absolute values are taken for the errors.

smaller values of h ($h = \frac{1}{32}$ and $\frac{1}{64}$), the error shows non-monotonic behaviour for degrees from 8 to 12 but is monotonic above and below these values. The non-monotonic behaviour that is conspicuous for smaller h is due to the round-off error proportional to $1/h^2$ for the second derivative. The numerical second derivative also provides accurate evaluation of the derivatives for most practical purposes.

The performance of integration and calculation of the integrand are clearly seen by checking the accuracy of the orthonormal integrals for the wavefunctions of the linear harmonic oscillator shown in table 1. The second column shows the orthonormal integrals obtained by using the central-difference integration formula for which the function is calculated exactly only at the mesh points. The numerical result demonstrates 15-digit accuracy of the central-difference integration formula with degree 8 and $h = \frac{1}{64}$. The third column shows numerical

Table 1. Orthonormal integrals $\langle\nu|\nu'\rangle$ of wavefunctions with quantum numbers ν and ν' of a linear harmonic oscillator. CDIF: central-difference integration formula with degree 8. GHE: Gauss–Hermite quadrature rule with exact integrand at 14 abscissas. GHI: Gauss–Hermite quadrature rule with interpolated integrand at 14 abscissas. MNIPGH: minimum number of integration points for the Gauss–Hermite quadrature rule for 15-digit accuracy.

$\langle\nu\|\nu'\rangle$	CDIF	GHE	GHI	MNIPGH
$\langle 0\|0\rangle$	1.000 000 000 000 000	1.000 000 000 000 000	1.000 000 000 000 000	1
$\langle 1\|1\rangle$	1.000 000 000 000 000	0.999 999 999 999 999	1.000 000 000 000 000	2
$\langle 2\|2\rangle$	1.000 000 000 000 000	1.000 000 000 000 000	1.000 000 000 000 000	3
$\langle 3\|3\rangle$	1.000 000 000 000 000	1.000 000 000 000 000	1.000 000 000 000 000	4
$\langle 4\|4\rangle$	0.999 999 999 999 999	0.999 999 999 999 999	1.000 000 000 000 000	5
$\langle 5\|5\rangle$	1.000 000 000 000 000	1.000 000 000 000 000	1.000 000 000 000 000	6
$\langle 6\|6\rangle$	1.000 000 000 000 000	1.000 000 000 000 000	1.000 000 000 000 000	6
$\langle 7\|7\rangle$	1.000 000 000 000 000	1.000 000 000 000 000	1.000 000 000 000 000	7
$\langle 8\|8\rangle$	0.999 999 999 999 999	1.000 000 000 000 000	1.000 000 000 000 000	8
$\langle 9\|9\rangle$	0.999 999 999 999 999	0.999 999 999 999 998	1.000 000 000 000 000	9
Others	0.000 000 000 000 000	0.000 000 000 000 000	0.000 000 000 000 000	2–12

Table 2. Matrix elements $\langle\nu|\xi|\nu'\rangle$ for wavefunctions with quantum numbers ν and ν' of a linear harmonic oscillator by using the central-difference integration formula (CDIF).

$\langle\nu\|\xi\|\nu'\rangle$	CDIF	Exact
$\langle 0\|\xi\|1\rangle$	7.071 067 811 865 47D−01	$0.5^{1/2} = 7.071\,067\,811\,865\,48$D−01
$\langle 1\|\xi\|2\rangle$	9.999 999 999 999 99D−01	1.0
$\langle 2\|\xi\|3\rangle$	1.224 744 871 391 59D+00	$1.5^{1/2} = 1.224\,744\,871\,391\,59$D+00
$\langle 3\|\xi\|4\rangle$	1.414 213 562 373 09D+00	$2.0^{1/2} = 1.414\,213\,562\,373\,10$D+00
$\langle 4\|\xi\|5\rangle$	1.581 138 830 084 19D+00	$2.5^{1/2} = 1.581\,138\,830\,084\,19$D+00
$\langle 5\|\xi\|6\rangle$	1.732 050 807 568 88D+00	$3.0^{1/2} = 1.732\,050\,807\,568\,88$D+00
$\langle 6\|\xi\|7\rangle$	1.870 828 693 386 97D+00	$3.5^{1/2} = 1.870\,828\,693\,386\,97$D+00
$\langle 7\|\xi\|8\rangle$	2.000 000 000 000 00D+00	2.0
$\langle 8\|\xi\|9\rangle$	2.121 320 343 559 64D+00	$4.5^{1/2} = 2.121\,320\,343\,559\,64$D+00
$\langle 9\|\xi\|10\rangle$	2.236 067 977 499 79D+00	$5.0^{1/2} = 2.236\,067\,977\,499\,79$D+00
Others	0.000 000 000 000 00	0

integration using the Gauss–Hermite quadrature rule with exactly evaluated functions at 14 abscissas. The 15-digit accuracy is clearly seen. The fourth column shows numerical integration by using the Gauss–Hermite quadrature rule with wavefunctions evaluated using polynomial interpolation at the abscissas. We obtained 15-digit accuracy, which also confirmed the interpolation with 15-digit accuracy. The fifth column shows the minimum number of integration points for the Gauss–Hermite quadrature rule for 15-digit accuracy. In addition to these, we evaluated the orthonormal integrals up to $\nu = 32$ which also show the same accuracy, but these are omitted for brevity.

The matrix elements for coordinate $\langle\nu|\xi^k|\nu'\rangle$, $k = 1, 2$, are shown in tables 2 and 3, respectively. The central-difference integration formula in this case also gives accurate integration as for the orthonormal integrals. The numerical integration provides both diagonal and off-diagonal matrix elements with the same accuracy, in contrast to the method that provides only diagonal matrix elements [12–20]. Further, we evaluated the matrix elements up to $\nu = 32$ which show the same accuracy, but are again omitted for brevity. In addition to these we also calculated matrix elements (not shown for brevity) for ξ^3 and ξ^4 which show the same high performance as for ξ and ξ^2.

Table 3. Matrix elements $\langle\nu|\xi^2|\nu'\rangle$ for wavefunctions with quantum numbers ν and ν' of a linear harmonic oscillator by using the central-difference integration formula (CDIF).

$\langle\nu\|\xi^2\|\nu'\rangle$	CDIF	Exact
$\langle 0\|\xi^2\|0\rangle$	5.000 000 000 000 00D−01	0.5
$\langle 0\|\xi^2\|2\rangle$	7.071 067 811 865 47D−01	$0.5^{1/2} = 7.071\,067\,811\,865\,48$D−01
$\langle 1\|\xi^2\|1\rangle$	1.500 000 000 000 00D+00	1.5
$\langle 1\|\xi^2\|3\rangle$	1.224 744 871 391 59D+00	$1.5^{1/2} = 1.224\,744\,871\,391\,59$D+00
$\langle 2\|\xi^2\|2\rangle$	2.500 000 000 000 00D+00	2.5
$\langle 2\|\xi^2\|4\rangle$	1.732 050 807 568 88D+00	$3.0^{1/2} = 1.732\,050\,807\,568\,88$D+00
$\langle 3\|\xi^2\|3\rangle$	3.500 000 000 000 00D+00	3.5
$\langle 3\|\xi^2\|5\rangle$	2.236 067 977 499 79D+00	$5.0^{1/2} = 2.236\,067\,977\,499\,79$D+00
$\langle 4\|\xi^2\|4\rangle$	4.500 000 000 000 00D+00	4.5
$\langle 4\|\xi^2\|6\rangle$	2.738 612 787 525 83D+00	$7.5^{1/2} = 2.738\,612\,787\,525\,83$D+00
$\langle 5\|\xi^2\|5\rangle$	5.500 000 000 000 00D+00	5.5
$\langle 5\|\xi^2\|7\rangle$	3.240 370 349 203 93D+00	$10.5^{1/2} = 3.240\,370\,349\,203\,93$D+00
$\langle 6\|\xi^2\|6\rangle$	6.500 000 000 000 00D+00	6.5
$\langle 6\|\xi^2\|8\rangle$	3.741 657 386 773 94D+00	$14.0^{1/2} = 3.741\,657\,386\,773\,94$D+00
$\langle 7\|\xi^2\|7\rangle$	7.500 000 000 000 00D+00	7.5
$\langle 7\|\xi^2\|9\rangle$	4.242 640 687 119 29D+00	$18.0^{1/2} = 4.242\,640\,687\,119\,28$D+00
$\langle 8\|\xi^2\|8\rangle$	8.500 000 000 000 00D+00	8.5
$\langle 8\|\xi^2\|10\rangle$	4.743 416 490 252 57D+00	$22.5^{1/2} = 4.743\,416\,490\,252\,57$D+00
$\langle 9\|\xi^2\|9\rangle$	9.500 000 000 000 00D+00	9.5
$\langle 9\|\xi^2\|11\rangle$	5.244 044 240 850 76D+00	$27.5^{1/2} = 5.244\,044\,240\,850\,76$D+00
Others	0.000 000 000 000 00	0

Table 4. Matrix elements $\langle\nu|\mathrm{d}/\mathrm{d}\xi|\nu'\rangle$ for wavefunctions with quantum numbers ν and ν' of a linear harmonic oscillator by using the central-difference integration formula.

$\langle\nu\|\mathrm{d}/\mathrm{d}\xi\|\nu'\rangle$	Numerical derivative	Analytic derivative	Exact
$\langle 0\|\mathrm{d}/\mathrm{d}\xi\|1\rangle$	7.071 067 811 865 47D−01	7.071 067 811 865 47D−01	$0.5^{1/2} = 7.071\,067\,811\,865\,48$D−01
$\langle 1\|\mathrm{d}/\mathrm{d}\xi\|2\rangle$	1.000 000 000 000 00D+00	1.000 000 000 000 00D+00	1.0
$\langle 2\|\mathrm{d}/\mathrm{d}\xi\|3\rangle$	1.224 744 871 391 59D+00	1.224 744 871 391 59D+00	$1.5^{1/2} = 1.224\,744\,871\,391\,59$D+00
$\langle 3\|\mathrm{d}/\mathrm{d}\xi\|4\rangle$	1.414 213 562 373 10D+00	1.414 213 562 373 09D+00	$2.0^{1/2} = 1.414\,213\,562\,373\,10$D+00
$\langle 4\|\mathrm{d}/\mathrm{d}\xi\|5\rangle$	1.581 138 830 084 19D+00	1.581 138 830 084 19D+00	$2.5^{1/2} = 1.581\,138\,830\,084\,19$D+00
$\langle 5\|\mathrm{d}/\mathrm{d}\xi\|6\rangle$	1.732 050 807 568 88D+00	1.732 050 807 568 88D+00	$3.0^{1/2} = 1.732\,050\,807\,568\,88$D+00
$\langle 6\|\mathrm{d}/\mathrm{d}\xi\|7\rangle$	1.870 828 693 386 97D+00	1.870 828 693 386 97D+00	$3.5^{1/2} = 1.870\,828\,693\,386\,97$D+00
$\langle 7\|\mathrm{d}/\mathrm{d}\xi\|8\rangle$	2.000 000 000 000 00D+00	2.000 000 000 000 00D+00	2.0
$\langle 8\|\mathrm{d}/\mathrm{d}\xi\|9\rangle$	2.121 320 343 559 64D+00	2.121 320 343 559 64D+00	$4.5^{1/2} = 2.121\,320\,343\,559\,64$D+00
$\langle 9\|\mathrm{d}/\mathrm{d}\xi\|10\rangle$	2.236 067 977 499 79D+00	2.236 067 977 499 79D+00	$5.0^{1/2} = 2.236\,067\,977\,499\,79$D+00
Others	0.000 000 000 000 00	0.000 000 000 000 00	0

We show in table 4 the matrix elements for the derivative $\langle\nu|\mathrm{d}/\mathrm{d}\xi|\nu'\rangle$ by using the central-difference integration formula. The third column, calculated with the analytic solution of the derivatives, indicates the accuracy of the central-difference integration formula in comparison with the exact results shown in the fourth column. The second column shows that the numerical differentiation at the mesh points is accurate.

The matrix elements for $\langle\nu|\xi|\nu'\rangle$ and $\langle\nu|\mathrm{d}/\mathrm{d}\xi|\nu'\rangle$ are the dipole and momentum matrix elements, respectively, in the optical transitions in quantum mechanics and the equality $\langle\nu|\xi|\nu'\rangle = \langle\nu|\mathrm{d}/\mathrm{d}\xi|\nu'\rangle$ holds to 15-digit accuracy according to tables 2 and 4.

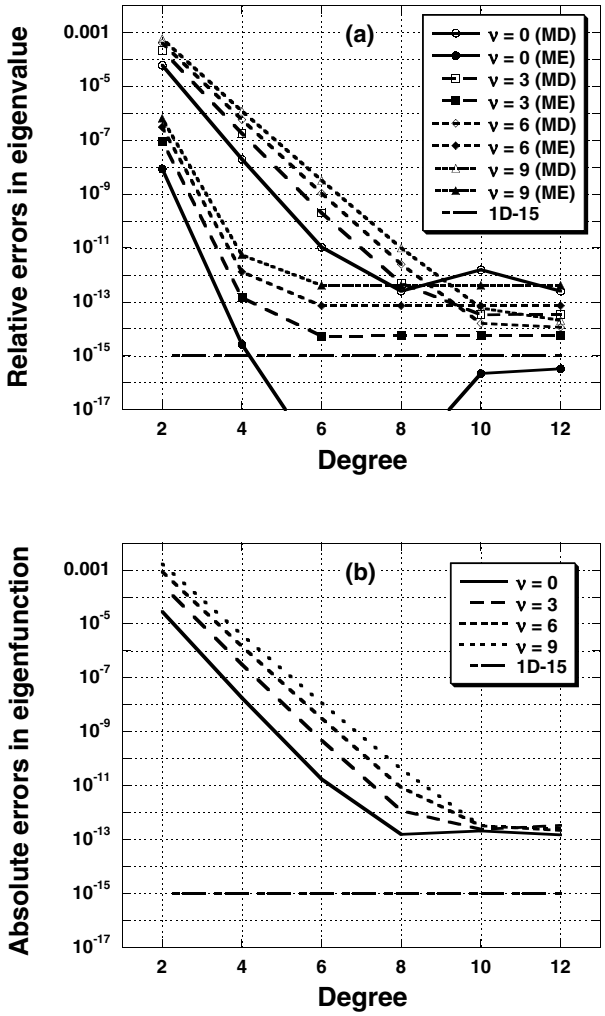

Figure 4. (a) Relative errors in eigenvalues for quantum numbers $\nu = 0$–9 as a function of degree n of the second derivative formulae and relative errors in the matrix elements E_ν. MD indicates the method of discretized matrix equation and ME denotes matrix elements. (b) Absolute errors in wavefunctions for $\nu = 0$–9 as a function of degree n of the second derivative formulae. Absolute values are taken for the errors.

We show in table 5 the matrix elements for the second derivative $\langle\nu|(\mathrm{d}/\mathrm{d}\xi)^2|\nu'\rangle$. The second column, calculated using the numerical derivatives, where the second derivative is calculated by using the first derivative twice, indicates the accuracy of the numerical derivative. The third column shows that the formula for the analytic second derivative at the mesh points coincides with the exact result. We also calculated the second derivative by using equation (10) with $m = 2$, which shows similar results.

The diagonal matrix elements for $\langle T\rangle = \langle\nu| - (\mathrm{d}/\mathrm{d}\xi)^2|\nu\rangle$ and $\langle V\rangle = \langle\nu|\xi^2|\nu\rangle$ are kinetic and potential energies, respectively, and the relation $\langle T\rangle = \langle V\rangle = \frac{1}{2}E_\nu$, $E_\nu = \langle\nu| - (\mathrm{d}/\mathrm{d}\xi)^2 + \xi^2|\nu\rangle/\langle\nu|\nu\rangle$, for the linear harmonic oscillator holds to 15-digit accuracy as shown in tables 3, 5 and 6.

Table 5. Matrix elements $\langle\nu|(\mathrm{d}/\mathrm{d}\xi)^2|\nu'\rangle$ for wavefunctions with quantum numbers ν and ν' of a linear harmonic oscillator by using the central-difference integration formula.

$\langle\nu\|(\mathrm{d}/\mathrm{d}\xi)^2\|\nu'\rangle$	Numerical derivative	Analytic derivative	Exact
$\langle 0\|(\mathrm{d}/\mathrm{d}\xi)^2\|0\rangle$	−5.000 000 000 000 00D−01	−5.000 000 000 000 00D−01	−0.5
$\langle 0\|(\mathrm{d}/\mathrm{d}\xi)^2\|2\rangle$	7.071 067 811 865 48D−01	7.071 067 811 865 48D−01	$0.5^{1/2}$ = 7.071 067 811 865 48D−01
$\langle 1\|(\mathrm{d}/\mathrm{d}\xi)^2\|1\rangle$	−1.500 000 000 000 00D+00	−1.500 000 000 000 00D+00	−1.5
$\langle 1\|(\mathrm{d}/\mathrm{d}\xi)^2\|3\rangle$	1.224 744 871 391 59D+00	1.224 744 871 391 59D+00	$1.5^{1/2}$ = 1.224 744 871 391 59D+00
$\langle 2\|(\mathrm{d}/\mathrm{d}\xi)^2\|2\rangle$	−2.500 000 000 000 00D+00	−2.500 000 000 000 00D+00	−2.5
$\langle 2\|(\mathrm{d}/\mathrm{d}\xi)^2\|4\rangle$	1.732 050 807 568 88D+00	1.732 050 807 568 88D+00	$3.0^{1/2}$ = 1.732 050 807 568 88D+00
$\langle 3\|(\mathrm{d}/\mathrm{d}\xi)^2\|3\rangle$	−3.500 000 000 000 00D+00	−3.500 000 000 000 00D+00	−3.5
$\langle 3\|(\mathrm{d}/\mathrm{d}\xi)^2\|5\rangle$	2.236 067 977 499 79D+00	2.236 067 977 499 79D+00	$5.0^{1/2}$ = 2.236 067 977 499 79D+00
$\langle 4\|(\mathrm{d}/\mathrm{d}\xi)^2\|4\rangle$	−4.500 000 000 000 00D+00	−4.500 000 000 000 00D+00	−4.5
$\langle 4\|(\mathrm{d}/\mathrm{d}\xi)^2\|6\rangle$	2.738 612 787 525 83D+00	2.738 612 787 525 83D+00	$7.5^{1/2}$ = 2.738 612 787 525 83D+00
$\langle 5\|(\mathrm{d}/\mathrm{d}\xi)^2\|5\rangle$	−5.500 000 000 000 00D+00	−5.500 000 000 000 00D+00	−5.5
$\langle 5\|(\mathrm{d}/\mathrm{d}\xi)^2\|7\rangle$	3.240 370 349 203 93D+00	3.240 370 349 203 93D+00	$10.5^{1/2}$ = 3.240 370 349 203 93D+00
$\langle 6\|(\mathrm{d}/\mathrm{d}\xi)^2\|6\rangle$	−6.500 000 000 000 00D+00	−6.500 000 000 000 00D+00	−6.5
$\langle 6\|(\mathrm{d}/\mathrm{d}\xi)^2\|8\rangle$	3.741 657 386 773 94D+00	3.741 657 386 773 94D+00	$14.0^{1/2}$ = 3.741 657 386 773 94D+00
$\langle 7\|(\mathrm{d}/\mathrm{d}\xi)^2\|7\rangle$	−7.500 000 000 000 00D+00	−7.500 000 000 000 00D+00	−7.5
$\langle 7\|(\mathrm{d}/\mathrm{d}\xi)^2\|9\rangle$	4.242 640 687 119 28D+00	4.242 640 687 119 28D+00	$18.0^{1/2}$ = 4.242 640 687 119 28*D*+00
$\langle 8\|(\mathrm{d}/\mathrm{d}\xi)^2\|8\rangle$	−8.499 999 999 999 99D+00	−8.500 000 000 000 00D+00	−8.5
$\langle 8\|(\mathrm{d}/\mathrm{d}\xi)^2\|10\rangle$	4.743 416 490 252 56D+00	4.743 416 490 252 57D+00	$22.5^{1/2}$ = 4.743 416 490 252 57*D*+00
$\langle 9\|(\mathrm{d}/\mathrm{d}\xi)^2\|9\rangle$	−9.500 000 000 000 00D+00	−9.500 000 000 000 00D+00	−9.5
$\langle 9\|(\mathrm{d}/\mathrm{d}\xi)^2\|11\rangle$	5.244 044 240 850 75D+00	5.244 044 240 850 76D+00	$27.5^{1/2}$ = 5.244 044 240 850 76D+00
Others	0.000 000 000 000 000	0.000 000 000 000 000	0

Table 6. Matrix elements $E_\nu = \langle\nu|H|\nu\rangle/\langle\nu|\nu\rangle = \langle\nu|-(\mathrm{d}/\mathrm{d}\xi)^2+U(\xi)|\nu\rangle/\langle\nu|\nu\rangle$ for wavefunctions with quantum number ν of a linear harmonic oscillator by using the central-difference integration formula.

Quantum no	Numerical derivative	Analytic derivative	Exact
0	1.000 000 000 000 00D+00	1.000 000 000 000 00D+00	1.0
1	3.000 000 000 000 00D+00	3.000 000 000 000 00D+00	3.0
2	5.000 000 000 000 00D+00	5.000 000 000 000 00D+00	5.0
3	7.000 000 000 000 00D+00	7.000 000 000 000 00D+00	7.0
4	9.000 000 000 000 00D+00	9.000 000 000 000 00D+00	9.0
5	1.100 000 000 000 00D+01	1.100 000 000 000 00D+01	11.0
6	1.300 000 000 000 00D+01	1.300 000 000 000 00D+01	13.0
7	1.500 000 000 000 00D+01	1.500 000 000 000 00D+01	15.0
8	1.700 000 000 000 00D+01	1.700 000 000 000 00D+01	17.0
9	1.900 000 000 000 00D+01	1.900 000 000 000 00D+01	19.0

Table 7. Eigenvalues of the discretized matrix equation and matrix elements $E_\nu = \langle\nu|-(\mathrm{d}/\mathrm{d}\xi)^2 + U(\xi)|\nu\rangle/\langle\nu|\nu\rangle$ for a wavefunction with quantum number ν of a linear harmonic oscillator by using the central-difference integration formula. The fifth column is the maximum of the absolute value of the absolute error for the wavefunctions (MAVAEWF).

Quantum no	Eigenvalue	E_ν	Exact	MAVAEWF
0	1.000 000 000 000 25D+00	1.000 000 000 000 00D+00	1.0	1.512D−13
1	3.000 000 000 000 27D+00	3.000 000 000 000 00D+00	3.0	2.476D−13
2	4.999 999 999 999 82D+00	4.999 999 999 999 99D+00	5.0	3.552D−13
3	7.000 000 000 000 25D+00	6.999 999 999 999 96D+00	7.0	3.413D−13
4	9.000 000 000 000 25D+00	8.999 999 999 999 87D+00	9.0	4.165D−13
5	1.100 000 000 000 02D+01	1.099 999 999 999 96D+01	11.0	2.358D−13
6	1.300 000 000 000 02D+01	1.299 999 999 999 91D+01	13.0	2.212D−13
7	1.499 999 999 999 93D+01	1.499 999 999 999 80D+01	15.0	3.189D−13
8	1.699 999 999 999 98D+01	1.699 999 999 999 59D+01	17.0	4.456D−13
9	1.900 000 000 000 04D+01	1.899 999 999 999 22D+01	19.0	2.548D−13

The result for the discretized matrix equation method for the linear harmonic oscillator, equations (21)–(24) and (4), is shown in figure 4. The relative errors of the eigenvalue decrease as a function of the degree n and converge to less than 5.0D-13 for n larger than or equal to 12 (figure 4(a)). The relative error increases for large ν where the error is larger than 5.0D-13. The relative errors of the matrix elements E_ν are smaller and decrease faster than those of the eigenvalues for errors larger than 5.0D-13 and converge at degree 6. These results indicate that the relative errors are less than 5.0D-13, substantially less in fact. The maximum absolute errors in the normalized eigenfunctions decrease monotonically as a function of the degree and converge below 5.0D-13 for degree n larger than or equal to 8, as shown in figure 4(b). Table 7 summarizes the results for degree 12, the whole interval $(-10.0, 10.0)$ and $h = \frac{1}{32}$. The accuracy of the eigenvalue in the second column is from 13 to 14 digits and that of the matrix element E_ν in the third column ranges from 13 to 15 digits and is of the same order as for the eigenvalue. The magnitude of the absolute errors for the normalized wavefunctions is less than 5.0D-13, as seen in the fifth column. In [51] the discretized matrix method of Numerov with defect correction was used for calculating eigenvalues of the linear harmonic oscillator and the relative error of the eigenvalues ranged widely from 1.3D-14 for $\nu = 0$ to 2.4D-12 for $\nu = 3$. In concluding this subsection it is noted again that analysis of the convergence for discretized matrix eigenvalues and matrix elements of the Hamiltonian provides a good cross-check for the eigenvalues.

4.2. Anharmonic oscillator

The second example is an anharmonic oscillator of the form $U(\xi) = \mu\xi^2 + \lambda\xi^4$, where μ and λ are constants [12, 14, 15, 18, 19, 23, 24, 52–70]. The potential has a single minimum for $\mu \geqslant 0$ but a double minimum for $\mu < 0$, symmetric with respect to $\xi = 0$ and the potential becomes infinite as $|\xi| \to \infty$ for positive λ. The number of bound states is infinite for this potential. The eigenvalue for the bound state has been frequently investigated for a wide range of physics applications and accurate eigenvalues were numerically obtained by using other methods of solution [52–70]. In order to illustrate the performance of our simple method, we take three typical cases for $(\mu, \lambda) = (0.0, 1.0)$, $(1.0, 1.0)$ and $(-1.0, 1.0)$ in table 8, where the degree and the whole interval are 12 and $(-4.843\,75, 4.843\,75)$ for the first two cases, and 14 and $(-4.531\,25, 4.531\,25)$ for the last one. The eigenvalues of the matrix equation and matrix elements E_ν are of 13-digit to 15-digit accuracy, which is much higher than the 7-digit accuracy obtained by using the discretized matrix equation with low degree [23, 24]. The accuracy of the present work is comparable to the best values ever reported [58, 60, 62, 66, 68, 69] in double-precision arithmetic operations. For the double-minimum case $(\mu, \lambda) = (-1.0, 1.0)$ we show ten states that probably have 13-digit or higher accuracy, though the results using other methods have not been shown.

The third example is an anharmonic oscillator of the form $U(\xi) = \xi^2 + \lambda\xi^2/(1 + g\xi^2)$, where λ and g are constants [18, 23, 24, 71–79] in the reduced units of $E_0 = \hbar^2/(2m\alpha^2)$ and of length $\xi = \alpha x$. The potential is symmetric with respect to $\xi = 0$ and infinite as $|\xi| \to \infty$. The number of bound states is also infinite for this potential. The eigenvalue for the bound state has been investigated in detail and exact eigenvalues were obtained for special combinations of λ, g and the quantum number ν [18, 23, 24, 71–79]. We take four typical cases for (λ, g, ν), indicated by the notation $(*)$ in table 9. The eigenvalues of the matrix are of 13-digit accuracy and E_ν are of 15-digit accuracy for degree 12, the whole interval $(-10.0, 10.0)$ and $h = \frac{1}{32}$; the accuracy is comparable to the best values ever reported [23, 75–79] in double-precision arithmetic operations. For another typical case, $\lambda = g = 1.0$, we show ten states whose eigenvalues and E_ν coincide with those in [78, 79] within the accuracy referred to therein.

4.3. Morse potential and modified Pöschl–Teller potential

The fourth example is the nonlinear Morse potential $U(x) = V_0(\mathrm{e}^{-2\alpha x} - 2\mathrm{e}^{-\alpha x})$ [3–5, 80]. The potential is non-symmetric with respect to $x = 0$ and has a finite range between $-V_0$ and zero for $x > 0$ and is infinite as $x \to -\infty$. The number of bound states is finite for this potential. The Schrödinger equation can also be reduced to dimensionless form by introducing units of energy $E_0 = \hbar^2/(2m\alpha^2)$ and of length $\xi = \alpha x$. The eigenvalue for the bound state with quantum number ν is given by [3–5]

$$\lambda_\nu = (E_\nu/E_0) = -(V_0/E_0)[1 - (\nu + 0.5)/(V_0/E_0)^{1/2}]^2 \tag{28}$$

where $\nu = 0, 1, 2, \ldots$ with $\nu < (V_0/E_0)^{1/2} - 0.5$. We show typical cases for V_0/E_0 in table 10, where the degree is 14 and $h = \frac{1}{32}$, the whole interval is $(-4.1875, 35.8125)$ for $V_0/E_0 = 1.0$, $(-3.781\,25, 27.468\,75)$ for 2.25, $(-3.281\,25, 21.718\,75)$ for 6.25 and $(-2.96, 22.64)$ for 12.25. The eigenvalues and the matrix elements of the Hamiltonian are of 13- to 15-digit accuracy.

Another form of the Morse potential [2, 6, 25, 51, 81–84] is $U(x) = D\{1 - \exp[-\alpha(x - x_0)]\}^2$ with $D = \omega_e^2/4\omega_e x_e$, $\alpha = (k\omega_e x_e)^{1/2}$ and $k = 1$, having the theoretical eigenvalues

$$E_\nu = \omega_e(\nu + \tfrac{1}{2}) - \omega_e x_e(\nu + \tfrac{1}{2})^2. \tag{29}$$

The eigenvalues and matrix elements of the Hamiltonian for the case $x_0 = 2.408\,73$, $\omega_e = 48.668\,88$ and $\omega_e x_e = 0.977\,888$ [25, 84], are of 13- to 15-digit accuracy for the degree

Table 8. Eigenvalues of the discretized matrix equation and matrix elements $E_\nu = \langle\nu| - (\mathrm{d}/\mathrm{d}\xi)^2 + U(\xi)|\nu\rangle/\langle\nu|\nu\rangle$ for a wavefunction with quantum number ν of a potential $V(\xi) = \mu\xi^2 + \lambda\xi^4$ by using the central-difference integration formula.

μ	λ	Quantum no	Eigenvalue	E_ν	Other methods
0.0	1.0	0	1.060 362 090 484 94D+00	1.060 362 090 484 18D+00	1.060 362 090 484 18D+00[a,b,c,d]
		1	3.799 673 029 799 24D+00	3.799 673 0298 014 0D+00	3.799 673 029 801 40D+00[a,b,c]
		2	7.455 697 937 987 76D+00	7.455 697 937 986 74D+00	7.455 697 937 986 74D+00[a,b]
		3	1.164 474 551 137 86D+01	1.164 474 551 137 82D+01	1.164 474 551 137 82D+01[a,b]
		4	1.626 182 601 885 11D+01	1.626 182 601 885 02D+01	1.626 182 601 885 02D+01[a]
		5	2.123 837 291 823 54D+01	2.123 837 291 823 59D+01	2.123 837 291 823 60D+01[a]
		6	2.652 847 118 368 03D+01	2.652 847 118 368 24D+01	2.652 847 118 368 25D+01[a]
		7	3.209 859 771 096 60D+01	3.209 859 771 096 80D+01	3.209 859 771 096 83D+01[a]
		8	3.792 300 102 703 42D+01	3.792 300 102 703 30D+01	3.792 300 102 703 40D+01[a]
		9	4.398 115 809 729 02D+01	4.398 115 809 728 74D+01	4.398 115 809 728 97D+01[a]
1.0	1.0	0	1.392 351 641 520 79D+00	1.392 351 641 530 29D+00	1.392 351 641 530 29D+00[a,b,c,e]
		1	4.648 812 704 209 47D+00	4.648 812 704 212 08D+00	4.648 812 704 212 08D+00[a,b,c,e]
		2	8.655 049 957 754 54D+00	8.655 049 957 759 32D+00	8.655 049 957 759 31D+00[a,b,e]
		3	1.315 680 389 804 50D+01	1.315 680 389 804 99D+01	1.315 680 389 804 99D+01[a,b,e]
		4	1.805 755 743 630 02D+01	1.805 755 743 630 32D+01	1.805 755 743 630 33D+01[a,e]
		5	2.329 744 145 121 87D+01	2.329 744 145 122 31D+01	2.329 744 145 122 32D+01[a,e]
		6	2.883 533 845 950 03D+01	2.883 533 845 950 41D+01	2.883 533 845 950 42D+01[a,e]
		7	3.464 084 832 110 68D+01	3.464 084 832 111 08D+01	3.464 084 832 111 13D+01[a,e]
		8	4.069 038 608 210 14D+01	4.069 038 608 210 51D+01	4.069 038 608 210 64D+01[a,e]
		9	4.696 500 950 567 40D+01	4.696 500 950 567 24D+01	4.696 500 950 567 55D+01[a,e]

Table 8. (Continued.)

μ	λ	Quantum no	Eigenvalue	E_v	Other methods
−1.0	1.0	0	6.576 530 051 780 60D−01	6.576 530 051 807 15D−01	6.576 530 051 807 15D−01[b,f]
		1	2.834 536 202 116 43D+00	2.834 536 202 119 30D+00	2.834 536 202 119 30D+00[b,f]
		2	6.163 901 256 958 67D+00	6.163 901 256 963 07D+00	
		3	1.003 864 612 070 77D+01	1.003 864 612 071 16D+01	
		4	1.437 240 650 467 45D+01	1.437 240 650 467 79D+01	
		5	1.908 571 468 502 16D+01	1.908 571 468 502 42D+01	
		6	2.412 807 549 278 05D+01	2.412 807 549 278 22D+01	
		7	2.946 285 591 419 97D+01	2.946 285 591 420 11D+01	
		8	3.506 214 903 107 54D+01	3.506 214 903 107 60D+01	
		9	4.090 385 627 182 25D+01	4.090 385 627 182 30D+01	

[a] Banerjee *et al* [60].
[b] Fernández *et al* [69].
[c] Schiffrer and Stanzial [68].
[d] Biswas *et al* [58].
[e] Banerjee [62].
[f] Basla *et al* [66].

Table 9. Eigenvalues of the discretized matrix equation and matrix elements $E_\nu = \langle\nu| - (\mathrm{d}/\mathrm{d}\xi)^2 + U(\xi)|\nu\rangle/\langle\nu|\nu\rangle$ for a wavefunction with quantum number ν of a potential $V(\xi) = \xi^2 + \lambda\xi^2/(1 + g\xi^2)$ by using the central-difference integration formula.

λ	g	Quantum no	Eigenvalue	E_ν	Other methods
−0.42	0.1	0	8.000 000 000 004 12D−01	8.000 000 000 000 00D−01	0.8[*,a]
		1	2.455 698 585 118 43D+00	2.455 698 585 119 10D+00	2.455 698 585 119[b]
		2	4.197 895 893 444 87D+00	4.197 895 893 444 28D+00	4.197 895 893 444[b]
		3	5.991 398 837 190 70D+00	5.991 398 837 189 80D+00	5.991 398 837 190[b]
		4	7.820 097 654 268 70D+00	7.820 097 654 268 44D+00	7.820 097 654 268[b]
		5	9.674 537 312 905 86D+00	9.674 537 312 906 14D+00	9.674 537 312 906[b]
−0.46	0.1	1	2.399 999 999 999 43D+00	2.400 000 000 000 00D+00	2.4[*,c]
−0.495 357 508 034 270	0.1	2	4.046 424 919 656 84D+00	4.046 424 919 657 30D+00	4.046 424 919 657 30[*,d]
−0.527 762 515 838 433	0.1	3	5.722 374 841 615 66D+00	5.722 374 841 615 66D+00	5.722 374 841 615 67[*,e]
1.0	1.0	0	1.232 350 723 405 27D+00	1.232 350 723 406 06D+00	1.232 350 723 406 06[f]
		1	3.507 388 348 905 61D+00	3.507 388 348 905 28D+00	3.507 388 348 905[b]
		2	5.589 778 933 736 18D+00	5.589 778 933 737 15D+00	5.589 778 933 736[b]
		3	7.648 201 241 718 89D+00	7.648 201 241 719 34D+00	7.648 201 241 723[b]
		4	9.684 042 015 229 18D+00	9.684 042 015 229 99D+00	9.684 042 015 230 17[f]
		5	1.171 223 747 020 79D+01	1.171 223 747 020 79D+01	
		6	1.373 324 101 210 73D+01	1.373 324 101 210 84D+01	
		7	1.575 063 879 714 55D+01	1.575 063 879 714 41D+01	
		8	1.776 477 910 142 13D+01	1.776 477 910 141 69D+01	
		9	1.977 689 487 169 51D+01	1.977 689 487 168 65D+01	

[*] Exact eigenvalue.
[a] Fack and Vanden Berghe [23] and Flessas [75].
[b] Fack *et al* [78].
[c] Fack and Vanden Berghe [23] and Varma [76].
[d] This result is calculated by using expressions in Fack and Vanden Berghe [23] and Flessas [75].
[e] This result is calculated by using expressions in Fack and Vanden Berghe [23] and Varma [76].
[f] Hodgson [79].

Table 10. Eigenvalues of the discretized matrix equation and matrix elements $E_v = \langle v| - (\mathrm{d}/\mathrm{d}\xi)^2 + U(\xi)|v\rangle/\langle v|v\rangle$ for a wavefunction with quantum number v of a Morse potential (A) $V(x) = V_0[\exp(-2\alpha x) - 2\exp(-\alpha x)]$ for depth V_0/E_0 and (B) $V(x) = D[1 - \exp(-\alpha(x - x_e))]^2$ by using the central-difference integration formula.

	Depth	Quantum no	Eigenvalue	E_v	Exact
(A)	1.0	0	−2.499 999 999 993 25D−01	−2.500 000 000 000 00D−01	−0.25
	2.25	0	−1.000 000 000 000 78D+00	−1.000 000 000 000 00D+00	−1.0
	6.25	0	−4.000 000 000 000 18D+00	−4.000 000 000 000 05D+00	−4.0
		1	−1.000 000 000 000 18D+00	−1.000 000 000 000 10D+00	−1.0
	12.25	0	−9.000 000 000 000 14D+00	−9.000 000 000 000 00D+00	−9.0
		1	−3.999 999 999 998 92D+00	−4.000 000 000 000 01D+00	−4.0
		2	−1.000 000 000 000 97D+00	−1.000 000 000 000 01D+00	−1.0
(B)		0	2.408 996 799 999 84D+01	2.408 996 800 000 00D+01	2.408 996 800 000 00D+01[a]
		1	7.080 307 200 000 88D+01	7.080 307 199 999 97D+01	7.080 307 200 000 00D+01[a]
		2	1.155 603 999 999 99D+02	1.155 603 999 999 99D+02	1.155 604 000 000 00D+02[a]
		3	1.583 619 519 999 96D+02	1.583 619 519 999 95D+02	1.583 619 520 000 00D+02[a]
		4	1.992 077 279 999 83D+02	1.992 0772 799 998 6D+02	1.992 077 280 000 00D+02[a]
		5	2.380 977 279 999 97D+02	2.380 977 279 999 68D+02	2.380 977 280 000 00D+02[a]
		6	2.750 319 520 000 07D+02	2.750 319 519 999 34D+02	2.750 319 520 000 00D+02[a]
		7	3.100 104 000 000 01D+02	3.100 103 999 998 81D+02	3.100 104 000 000 00D+02[a]
		8	3.430 330 719 999 89D+02	3.430 330 719 998 04D+02	3.430 330 720 000 00D+02[a]
		9	3.740 999 680 000 06D+02	3.740 999 679 997 00D+02	3.740 999 680 000 00D+02[a]
		10	4.032 110 880 000 00D+02	4.032 110 879 995 71D+02	4.032 110 880 000 00D+02[a]

[a] Dagher and Kobeissi [84].

Table 11. Eigenvalues of the discretized matrix equation and matrix elements $E_\nu = \langle\nu|-(\mathrm{d}/\mathrm{d}\xi)^2 + U(\xi)|\nu\rangle/\langle\nu|\nu\rangle$ for a wavefunction with quantum number ν of a modified Pöschl–Teller potential for depth V_0/E_0 by using the central-difference integration formula.

Depth	Quantum no.	Eigenvalue	E_ν	Exact
1.0	0	−3.819 660 112 500 28D−01	−3.819 660 112 500 98D−01	−3.819 660 112 501 05D−01
2.0	0	−1.000 000 000 000 22D+00	−1.000 000 000 000 00D+00	−1.0
6.0	0	−4.000 000 000 000 23D+00	−4.000 000 000 000 02D+00	−4.0
	1	−1.000 000 000 002 50D+00	−1.000 000 000 000 04D+00	−1.0
12.0	0	−9.000 000 000 001 13D+00	−9.000 000 000 000 15D+00	−9.0
	1	−4.000 000 000 000 68D+00	−4.000 000 000 000 55D+00	−4.0
	2	−1.000 000 000 001 58D−01	−1.000 000 000 000 66D+00	−1.0

larger than or equal to 10, the whole interval (1.119 6675, 6.432 1675) and $h = \frac{1}{128}$. In [25] the relative error for E_{10} was of the order of 1.0D-8 for degree 10, the whole interval (0.8, 4.96) and $h = 0.01$; we obtain the very close result with relative error 3.4D-8 for the same condition. However, by moving the whole interval to (1.12, 5.28) we obtain the relative error 2.8D-11 for E_{10} and other eigenvalues are also improved. Thus it is important to choose appropriately the whole interval. In [51] the discretized matrix method of Numerov with defect correction was used for calculating eigenvalues of the Morse potential. The relative error of the eigenvalues ranged widely, from 5.0D-14 for $\nu = 0$ to 8.6D-10 for $\nu = 9$.

The fifth example is a symmetric nonlinear potential hole of the form $U(x) = -V_0/\cosh^2(\alpha x)$, where V_0 is a constant [3–5]. The potential is symmetric with respect to $x = 0$ and has a finite value between $-V_0$ and zero. The number of bound states is also finite for this potential. The Schrödinger equation can be reduced to dimensionless form by introducing units of energy $E_0 = \hbar^2/(2m\alpha^2)$ and of length $\xi = \alpha x$. The eigenvalue for the bound state with quantum number ν is given by

$$\lambda_\nu = (E_\nu/E_0) = -\{-(1+2\nu) + [1 + 4(V_0/E_0)]^{1/2}\}^2/4 \tag{30}$$

where $n = 0, 1, 2, \ldots$ with $\nu < \{-1 + [1 + 4(V_0/E_0)]^{1/2}\}/2$, and the wavefunction is given in [3–5]. We show typical cases for V_0/E_0 in table 11, where the degree is 14, the whole interval and h are $(-26.7, 26.7)$ and $\frac{1}{24}$ for $V_0/E_0 = 1.0$, while the other corresponding values are $(-20.0, 20.0)$ and $\frac{1}{32}$ for $V_0/E_0 = 2.0$, 6.0 and 12.0. Since the eigenfunction extends widely for the finite-depth potentials, the whole interval should also be correspondingly wider. The eigenvalues and matrix elements of the Hamiltonian are of 13- to 15-digit accuracy.

5. Conclusion

We have developed a method for accurate numerical calculation of matrix elements in quantum mechanics in one dimension. Increasing the degree of the classical formulae yields fruitful results, i.e. high precision for interpolation, derivative, integration and solution of the eigenvalue problem of ordinary differential equations. We believe the method presented here is the most concise and accurate available.

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Appendix. Derivation of the central-difference integration formula

Let a function $y = f(x)$ be given in tabular form at discrete and distinct $(n + 1)$ points $y_k = f(x_k)$, centred at x_i, $k = i - (n/2), i - (n/2) + 1, \ldots, i - 1, i, i + 1, \ldots, i + (n/2)$, where n is an even number and x_k is arranged in increasing order. The integral over the three central points with interval $[x_{i-1}, x_{i+1}]$ is given in terms of the central difference $\delta^n f_i$ as

$$\int_{x_{i-1}}^{x_{i+1}} f(x)\,\mathrm{d}x = 2h[f_i + \tfrac{1}{6}\delta^2 f_i - \tfrac{1}{180}\delta^4 f_i + \tfrac{1}{1512}\delta^6 f_i - \tfrac{23}{226\,800}\delta^8 f_i + \cdots]. \tag{A.1}$$

This formula can be obtained by using the operational method for the central-difference integration formula [28, 85] or by integrating Stirling's formula [9]. Applying the formula of the central difference [30]

$$\delta^n f_i = \sum_{k=0}^{n} (-1)^k [n!/k!(n-k)!] f_{i+(n/2)-k} \tag{A.2}$$

to the right-hand side of equation (A.1), we obtain the integration formula containing terms up to $\delta^n f_i$ for $n = 6$ and 8:

$$\int_{x_{i-1}}^{x_{i+1}} f(x)\,\mathrm{d}x = (h/3780)[5 f_{i-3} - 72 f_{i-2} + 1503 f_{i-1} + 4688 f_i + 1503 f_{i+1} - 72 f_{i+2} + 5 f_{i+3}] + \mathrm{O}(h^9) \tag{A.3}$$

$$\int_{x_{i-1}}^{x_{i+1}} f(x)\,\mathrm{d}x = (h/113400)[-23 f_{i-4} + 334 f_{i-3} - 2804 f_{i-2} + 46378 f_{i-1} + 139\,030 f_i + 463\,78 f_{i+1} - 2804 f_{i+2} + 334 f_{i+3} - 23 f_{i+4}] + \mathrm{O}(h^{11}). \tag{A.4}$$

The formulae for $n = 2$ and 4 are shown in [9].

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