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A New Method for the Solution of the Schrödinger Equation

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We approximate the potential in the one-dimensional Schrödinger equation by a step function with a finite number of steps. In each step, the resulting differential equation has constant coefficients and is integrated exactly in terms of circular or hyperbolic functions. The solutions are then matched at the interface of each layer to construct the eigenfunctions in the whole domain. Unique features of the numerical method are: (a) All the eigenfunctions and eigenvalues are obtained with the same absolute accuracy for the same number of steps in the potential; (b) any desired number of eigenvalues and eigenfunctions are obtained in one single pass without any need to supply initial guesses for the eigenvalues; (c) for any fixed number of steps in the potential, we obtain in principle the whole infinite spectrum of eigenvalues and eigenfunctions.

1. INTRODUCTION

We present a method for the solution of the one-dimensional Schrödinger equation which is quite simple both from a conceptual and from a practical point of view.

The potential is approximated by a step function with an arbitrary but finite number of steps. In each step, the resulting differential equation has constant coefficients and is integrated exactly in terms of circular or hyperbolic functions. The solutions are then matched at the interface of each layer in order to obtain the eigenfunctions in the whole domain. The only idea involved is the very familiar one in Quantum Mechanics of matching the Schrödinger equation solutions at the interface of square potential barriers used, for example, in barrier penetration problems. The contribution of this work is essentially the implementation and testing of a numerical algorithm which solves the Schrödinger equation for a step potential function with an arbitrary number of steps.

The method has been tested in a variety of problems and the numerical results obtained are quite good. The input required for its implementation is only a numerical table of the potential, no initial guesses or iterates of the eigenvalues are necessary. The computer program yields in one single pass any desired number of

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eigenvalues, the corresponding eigenfunctions and their nodes. Further, the eigenvalues are obtained independently from the eigenfunctions, so that if only the eigenvalues are desired, the computing time can be reduced substantially.

An essential difference relative to the more conventional methods can be pointed out. In the method proposed, the potential is approximated by a step function, but once the approximate problem is obtained, it is integrated *exactly*. Therefore, the higher eigenvalues and eigenfunctions should be roughly as accurate as the fundamental eigenvalue and eigenfunction because all eigenfunctions are equally exact solutions to a given problem (i.e., they are written down explicitly in terms of circular and hyperbolic functions). This expectation is indeed confirmed by the numerical results.

In the more conventional methods, such as Rayleigh-Ritz ([1], [2]) or finite-difference methods ([3], [4]), it is necessary to increase progressively the number of mesh points in order to compute higher eigenvalues and eigenfunctions with the same given accuracy. Blatt [4] states that the number of mesh points needed in a finite-difference scheme must be roughly proportional to the number of nodes of the eigenfunction, in order to compute it with a given accuracy. This is also the case for Rayleigh-Ritz methods [1]. The reasons for this are that the eigenfunctions are *approximations* to the solutions of a given problem. Clearly, as the higher eigenfunctions oscillate more rapidly, as their order increases, more mesh points are needed in any approximation scheme to compute them with a given accuracy.

It will become apparent later that the approximation of the potential by a step function is central to our method. Indeed, for problems with very deep and rapidly varying potential wells, the use of the elementary addition formulas for the circular and hyperbolic functions is essential for simple and successful implementation of the numerical calculations.

2. Statement of the Problem

The one-dimensional Schrödinger equation is written in the following dimensionless form:

$$d^2y/dx^2 - V(x)\,y + Ey = 0, \tag{1}$$

where $V(x)$ is the potential function and E the energy eigenvalue. For the bound states in central field problems, $V(x)$ is infinite at the origin $x = 0$, has a negative minimum for some $x = a$, and then approaches zero asymptotically as $x \to \infty$. We will also consider problems for symmetric potential wells with infinitely high walls, because the method is quite general and can be equally applied in both situations. Indeed, from a practical point of view, Schrödinger equation will be treated as a Sturm-Liouville problem (i.e., the calculations are restricted to a

finite domain) and, therefore, the character of the potential function $V(x)$ is of secondary importance with respect to the computations. To fix ideas, we will restrict the discussion to Eq. (1) with the following boundary conditions

$$y(0) = y(L) = 0, \tag{2}$$

although the generalization to other homogeneous boundary conditions is immediate. The boundary conditions (2) are rigorous for a potential well problem with infinitely high walls; for a central field problem, it is usual to approximate the right boundary condition that the eigenfunctions remain finite for $x \to \infty$ by taking a suitably large L in (2) ([2], [3]). This is an obvious approximation, because for a large enough L, the eigenfunctions reach infinitesimally small values anyway.

3. Analytical Aspects

We define the approximate problem to (1) and (2) in the following way:

$$V(x) \approx \begin{cases} V_1 & 0 < x < x_1 \\ V_2 & x_1 < x < x_2 \\ \cdots & \cdots \\ V_n & x_{n-1} < x < x_n = L. \end{cases} \tag{3}$$

In (3), the constant values $V_1, V_2, \ldots, V_n$ are to be determined by approximating an analytical potential $V(x)$, if available, by a step function in a suitable way that does not need to be specified now. It suffices only to state that no matter what scheme we choose (there are an infinite variety of them), the potential can be approximated with arbitrary accuracy, $O(h)$, if we take a sufficiently small step width $h = x_i - x_{i-1}$ [5]. Therefore, we can define an approximate problem that will approach the exact problem as closely as we wish. Obviously, the approximation (3) does not require that the potential be known analytically.

Once a given number of potential steps is chosen, the approximate problem is solved exactly in terms of the elementary circular and hyperbolic functions. We, thus, might expect that the accuracy obtained will be roughly the same for all eigenvalues and eigenfunctions. This expectation is confirmed by the numerical results obtained.

In each region or layer i, the approximate problem reads

$$\begin{gathered} d^2y/dx^2 + (E - V_i)\, y = 0. \\ i = 1, 2, \ldots, n. \end{gathered} \tag{4}$$

It is convenient to define

$$\alpha_i \equiv E - V_i, \qquad \beta_i^2 \equiv |\, \alpha_i \,|, \tag{5}$$

so that the solution to (4) is

$$y = A_i F(\beta_i x) + B_i G(\beta_i x), \qquad i = 2, 3, \ldots, n-1, \tag{6}$$

TABLE I
Solutions of Eq. (4)

α_i	<0	$=0$	>0
$F(\beta_i x)$	$\cosh(\beta_i x)$	1	$\cos(\beta_i x)$
$G(\beta_i x)$	$\beta_i^{-1}\sinh(\beta_i x)$	x	$\beta_i^{-1}\sin(\beta_i x)$

where F and G are given in Table I, and A_i and B_i are integration constants. These elementary solutions express the well-known fact that the Schrödinger equation solutions are oscillatory within the region defined by the two classical turning points and exponential outside. The classical turning points are defined by

$$\alpha_i \equiv E - V_i = 0, \tag{7}$$

that is, they are those where the total energy equals the potential energy. We will show later that the turning points do not introduce any difficulty in the method, and, thus, they do not require special treatment as is for example the case in the *WKB* approximation. In order to satisfy the boundary conditions (2), the solutions in the boundary regions 1 and n are given, respectively, as follows:

$$y = B_1 G(\beta_1 x), \qquad y = B_n G[\beta_n(x - L)], \tag{8}$$

where G is defined also in Table I, and B_1 and B_n are the integration constants.

The procedure is now straightforward conceptually, although the actual algebra might get complicated. To solve the problem, we need to determine the integration constants A_i and B_i. This is done by matching the solution and its derivative at the interfaces. Thus, we obtain

$$\begin{aligned}
&G(\beta_1 x_1)\, B_1 - F(\beta_2 x_1)\, A_2 - G(\beta_2 x_1)\, B_2 = 0;\\
&G'(\beta_1 x_1)\, B_1 - F'(\beta_2 x_1)\, A_2 - G'(\beta_2 x_1)\, B_2 = 0;\\
&F(\beta_2 x_2)\, A_2 + G(\beta_2 x_2)\, B_2 - F(\beta_3 x_2)\, A_3 - G(\beta_3 x_2)\, B_3 = 0;\\
&F'(\beta_2 x_2)\, A_2 + G'(\beta_2 x_2)\, B_2 - F'(\beta_3 x_2)\, A_3 - G'(\beta_3 x_2)\, B_3 = 0;\\
&\qquad\qquad \cdots\\
&F(\beta_{n-1} x_{n-1})\, A_{n-1} + G(\beta_{n-1} x_{n-1})\, B_{n-1} - G[\beta_n(x_{n-1} - L)]\, B_n = 0;\\
&F'(\beta_{n-1} x_{n-1})\, A_{n-1} + G'(\beta_{n-1} x_{n-1})\, B_{n-1} - G'[\beta_n(x_{n-1} - L)]\, B_n = 0.
\end{aligned} \tag{9}$$

In (9), the primes designate the derivatives of the functions evaluated at the interfaces. Equations (9) are a homogeneous system of $2n - 2$ equations with $2n - 2$ unknowns (A_i, $i = 2, 3, \ldots, n-1$; B_i, $i = 1, 2, \ldots, n$). The condition for the existence of a nontrivial solution is that the determinant of the coefficients be equal to zero. Explicitly:

$$
|A| =
\begin{vmatrix}
G(\beta_1 x_1) & -F(\beta_2 x_1) & -G(\beta_2 x_1) & & & & \\
G'(\beta_1 x_1) & -F'(\beta_2 x_1) & -G'(\beta_2 x_1) & & & & \\
 & F(\beta_2 x_2) & G(\beta_2 x_2) & -F(\beta_3 x_2) & -G(\beta_3 x_2) & & \\
 & F'(\beta_2 x_2) & G'(\beta_2 x_2) & -F'(\beta_3 x_2) & -G'(\beta_3 x_2) & & \\
 & & & \ddots & & & \\
 & & & & & -G[\beta_n(x_{n-1} - L)] & \\
 & & & & & -G'[\beta_n(x_{n-1} - L)] &
\end{vmatrix} = 0. \tag{10}
$$

The roots of this determinant equation are the eigenvalues of the approximate problem, (1), (2), and (3). For each eigenvalue, there is a nontrivial solution for A_i, B_i that defines the corresponding eigenfunction. In what follows it is convenient to think of $|A|$ as a function of a real variable, $f(E) \equiv |A|$.

It is important to point out the essential difference between system (9) and those obtained in Rayleigh-Ritz or finite difference methods. In the latter, the homogeneous systems obtained are *algebraic* while system (9) is *transcendental.* Thus, an algebraic system of order n can yield in principle only the first n eigenvalues and eigenfunctions, while system (9), for any order n, contains the whole infinite spectrum of eigenvalues and eigenfunctions, because the determinant Eq. (10) is a transcendental equation and has always an infinite number of real roots. The fact that all the roots are real is guaranteed because (1), (2) with the approximation (3) is a Sturm-Liouville system [6].

4. Numerical Method

In this section, we present the analysis carried out in order to implement the numerical solution of system (9). We first focus in the matrix algebra analysis of the determinant Eq. (10), and then discuss the computation of the eigenfunctions. The reader might postpone a detailed study of this section without losing track of the essential features of the method.

A. The Eigenvalue Equation

Equation (10) will be referred to as the eigenvalue equation. We have already stated that it has an infinite number of real roots that are the bound state eigenvalues of the approximate problem (1), (2), and (3). For reasons that will become immediately apparent, it has been found convenient to translate the last column of the determinant (10) to the second place. Obviously, the roots of (10) are not affected by this. In this way, (10) becomes

$$\begin{vmatrix} \begin{pmatrix} G(\beta_1 x_1) & 0 \\ G'(\beta_1 x_1) & 0 \end{pmatrix} & \begin{pmatrix} -F(\beta_2 x_1) & -G(\beta_2 x_1) \\ -F'(\beta_2 x_1) & -G'(\beta_2 x_1) \end{pmatrix} & \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} & \cdots & \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \\ \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} & \begin{pmatrix} F(\beta_2 x_2) & G(\beta_2 x_2) \\ F'(\beta_2 x_2) & G'(\beta_2 x_2) \end{pmatrix} & \begin{pmatrix} -F(\beta_3 x_2) & -G(\beta_3 x_2) \\ -F'(\beta_3 x_2) & -G'(\beta_3 x_2) \end{pmatrix} & \cdots & \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} \\ \cdots & \cdots & & & \cdots \\ \begin{pmatrix} 0 & -G[\beta_n(x_{n-1} - L)] \\ 0 & -G'[\beta_n(x_{n-1} - L)] \end{pmatrix} & \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 0 \\ 0 & 0 \end{pmatrix} & \cdots & \begin{pmatrix} F(\beta_{n-1} x_{n-1}) & G(\beta_{n-1} x_{n-1}) \\ F'(\beta_{n-1} x_{n-1}) & G'(\beta_{n-1} x_{n-1}) \end{pmatrix} \end{vmatrix} = 0. \tag{11}$$

The elements in the determinant in (11) have been grouped in 2×2 matrices. It should be noted that, with the exception of the matrices corresponding to the first and last regions, all matrices are of the same form and refer to a single region i (specified by β_i) and a single interface. We can now write (11) in compact matrix notation:

$$|A| = \begin{vmatrix} A_{11} & -A_{12} & 0 & \cdots & 0 \\ 0 & A_{22} & -A_{23} & \cdots & 0 \\ 0 & 0 & \ddots & \ddots & -A_{n-2,n-1} \\ A_{n-1,1} & 0 & 0 & \cdots & A_{n-1,n-1} \end{vmatrix} = 0, \tag{12}$$

where the elements of the partitioned matrix A are the 2×2 matrices appearing in (11), and zero designates the null 2×2 matrix. Explicitly, the notation in (12) is

$$A_{11} = \begin{pmatrix} G(\beta_1 x_1) & 0 \\ G'(\beta_1 x_1) & 0 \end{pmatrix}, \qquad A_{n-1,1} = \begin{pmatrix} 0 & -G[\beta_n(x_{n-1} - L)] \\ 0 & -G'[\beta_n(x_{n-1} - L)] \end{pmatrix},$$
$$A_{ij} = \begin{pmatrix} F(\beta_j x_i) & G(\beta_j x_i) \\ F'(\beta_j x_i) & G'(\beta_j x_i) \end{pmatrix}. \tag{13}$$

It is a known result of matrix algebra that the determinant of A does not change if its last column is post-multiplied by $-A_{n-1,n-1}^{-1}A_{n-1,1}$, and the result added to the first column [7]. In this way, we get

$$|A| = \begin{vmatrix} A_{11} & -A_{12} & 0 & \cdots & 0 \\ 0 & A_{22} & -A_{23} & \cdots & 0 \\ \vdots & & \ddots & \ddots & \\ A_{n-2,n-1}A_{n-1,n-1}^{-1}A_{n-1,1} & 0 & 0 & \cdots & -A_{n-2,n-1} \\ 0 & 0 & 0 & \cdots & A_{n-1,n-1} \end{vmatrix} = 0. \tag{14}$$

Expanding the determinant by the last row gives

$$|A| = |A_{n-1,n-1}| \times \begin{vmatrix} A_{11} & -A_{12} & 0 & \cdots & 0 \\ 0 & A_{22} & -A_{23} & \cdots & 0 \\ & & \ddots & \ddots & \\ 0 & 0 & A_{n-3,n-3} & & -A_{n-3,n-2} \\ A_{n-2,n-1}A_{n-1,n-1}^{-1}A_{n-1,1} & 0 & 0 & \cdots & A_{n-2,n-2} \end{vmatrix} = 0. \tag{15}$$

The second determinant in the right side of (15) has the same form as the original determinant in Eq. (12), i.e., the only nonzero elements are those in the main diagonal, the upper diagonal and the lonely first element of the last row. Therefore, the process used is recursive, and is applied $n-2$ times to reduce the original eigenvalue Eq. (12) to the form

$$|A| = |A_{n-1,n-1}| \cdots |A_{22}| \times |A_{11} + A_{12}A_{22}^{-1}A_{23}A_{33}^{-1} \cdots A_{n-2,n-1}A_{n-1,n-1}^{-1}A_{n-1,1}| = 0. \tag{16}$$

From Eq. (13) and Table I, it is clear that

$$|A_{ii}| = 1, \qquad i = 2, 3, \ldots, n-1, \tag{17}$$

regardless of the value and sign of α_i. Therefore, Eq. (16) reduces finally to

$$|A| = |A_{11} + A_{12}A_{22}^{-1}A_{23}A_{33}^{-1} \cdots A_{n-2,n-1}A_{n-1,n-1}^{-1}A_{n-1,1}| = 0. \tag{18}$$

We have, therefore, reduced the evaluation of the determinant of a $(2n-2) \times (2n-2)$ matrix in (10) to that of the 2×2 matrix in the right side of (18).

It is necessary now to point out the considerable importance of having approximated the potential by a step function, so that all the elements in the matrices A_{ij} in (18) are given in terms of the elementary circular and hyperbolic functions [8]. Consider a bound state eigenvalue corresponding to an eigenfunction with

two turning points. In the classically forbidden regions, the eigenfunction behaves exponentially, that is, Eq. (5),

$$\alpha_i \equiv E - V_i < 0. \tag{19}$$

In our method, the eigenfunction is expressed in these regions in terms of hyperbolic functions, reflecting their exponential behavior (see Table I). It is a well-known difficulty in numerical methods (see [4]) that scaling problems (underflows) occur when computing the eigenfunctions away from the turning points. This is because in the classically forbidden region, the eigenfunction might be many orders of magnitude smaller than in the allowed region. Indeed, the situation is similar to that occurring in boundary layer problems, and if there were a need to compute the eigenfunction accurately away from a turning point (e.g., in a barrier penetration problem such as in alpha decay), then special treatment is required for this region [9]. Our method does not present these difficulties, indeed, it is uniformly valid, both in the classically allowed and forbidden regions, for problems where the potential wells are extremely deep. In what follows, we refer to these problems as asymptotic problems. The reasons can be understood by an examination of (18). Consider the nonsingular matrix in (18) furthest to the right of the turning point; see also (13) and Table I,

$$A_{n-2,n-1} = \begin{pmatrix} \cosh \beta_{n-1}x_{n-2} & \sinh(\beta_{n-1}x_{n-2})/\beta_{n-1} \\ \beta_{n-1} \sinh \beta_{n-1}x_{n-2} & \cosh \beta_{n-1}x_{n-2} \end{pmatrix}. \tag{20}$$

The scaling problems referred to above are reflected in the fact that in typical Quantum Mechanics problems, the arguments of the hyperbolic functions in (20) can grow quite big, say in excess of 100. It is clear that we would then be in trouble because

$$\sinh 100 \to \cosh 100 \to e^{100}/2. \tag{21}$$

Indeed, while multiplying numerically the 2×2 matrices in (18), in a direct evaluation of the determinant $| A | \equiv f(E)$, differences such as $\sinh 100 - \cosh 100$ must be evaluated numerically and are returned, of course, as zero. That is, in asymptotic situations, a direct evaluation of $| A | \equiv f(E)$ gives identically the result

$$| A | \equiv f(E) \equiv 0, \tag{22}$$

for E in the range of interest. However, except for the two singular matrices A_{11} and $A_{n-1,1}$, where the arguments of the hyperbolic functions are $O(1)$, we can group the matrices in (18) as follows:

$$A_{i-1,i}A_{ii}^{-1} = \begin{pmatrix} \cosh \beta_i(x_i - x_{i-1}) & -\sinh[\beta_i(x_i - x_{i-1})]/\beta_i \\ -\beta_i \sinh \beta_i(x_i - x_{i-1}) & \cosh \beta_i(x_i - x_{i-1}) \end{pmatrix}, \tag{23}$$

for the classically forbidden region outside the turning points, and

$$A_{i-1,i}A_{ii}^{-1} = \begin{pmatrix} \cos\beta_i(x_i - x_{i-1}) & -\sin[\beta_i(x_i - x_{i-1})]/\beta_i \\ \beta_i \sin\beta_i(x_i - x_{i-1}) & \cos\beta_i(x_i - x_{i-1}) \end{pmatrix} \tag{24}$$

for the allowed region inside. The expressions (23) and (24) were obtained by performing the matrix multiplications and using the elementary addition formulas for the circular and hyperbolic functions. This simple manipulation has, thus, eliminated in one stroke all the scaling difficulties connected with the eigenvalue equation, because the arguments of the hyperbolic functions have been reduced by at least two orders of magnitude with respect to those in (20) (for example, if the potential is approximated by 50 steps, $x_i - x_{i-1} = h < x_i/50$). We feel that the analytical elimination of the scaling difficulties has obvious advantages over a numerical treatment. It is doubtful that a similar result could have been obtained using a more refined approximation to the potential such as that pointed out in [8].

We conclude this section with a brief description of the numerical method used to find the roots of the determinant Eq. (18), with the matrices grouped as shown in (23) and (24). These roots are approximations to the energy eigenvalues for the bound states. It is useful to think of $|A|$ in (18) simply as a function of a real variable $f(E)$,

$$f(E) \equiv |A|, \tag{25}$$

whose zeros are to be determined numerically. The eigenvalue search is greatly facilitated by the fact that all eigenvaules are bounded from below by the minimum value of the potential ([10], [11])

$$E_n \geqslant V_{\min}. \tag{26}$$

In asymptotic problems with very deep potential wells, the fundamental energy eigenvalue approaches asymptotically the potential minimum [11],

$$E_0 \to V_{\min}. \tag{27}$$

We wrote a basic rootfinder subroutine *ROOTF* that computes the argument function $f(E)$ in a predetermined number of points in a range

$$V_{\min} < E < E_{\text{right}}, \tag{28}$$

where E_{right} is arbitrary and is to be chosen sufficiently to the right of $V_{\min}$ depending on how many eigenvalues are desired. Whenever a change of sign of the function $f(E)$ at two successive points is detected, *ROOTF* obtains the root by Mueller's iteration method [12]. Once the desired accuracy for the root is obtained,

ROOTF goes on evaluating the function toward the right until the next zero is detected. The search is terminated when the range (28) is scanned completely or when a predetermined number of eigenvalues has been found.

B. Computation of the Eigenfunctions

It has been found convenient to write System (9) in matrix notation in the following form:

$$\begin{aligned}
A_{11}\mathbf{c}_1 - A_{12}\mathbf{c}_2 &= 0 \\
A_{22}\mathbf{c}_2 - A_{23}\mathbf{c}_3 &= 0 \\
A_{33}\mathbf{c}_3 - A_{34}\mathbf{c}_4 &= 0 \\
&\cdots \\
A_{n-2,n-2}\mathbf{c}_{n-2} - A_{n-2,n-1}\mathbf{c}_{n-1} &= 0 \\
A_{n-1,1}\mathbf{c}_1 + A_{n-1,n-1}\mathbf{c}_{n-1} &= 0,
\end{aligned} \tag{29}$$

where A_{ij} are the 2×2 matrices given in (13) and $\mathbf{c}_i$ are the following two-row vectors:

$$\mathbf{c}_1 = \begin{pmatrix} B_1 \\ B_n \end{pmatrix}, \qquad \mathbf{c}_i = \begin{pmatrix} A_i \\ B_i \end{pmatrix}, \qquad i = 2, 3, \ldots, n-1. \tag{30}$$

The components of the vector $\mathbf{c}_1$ are the coefficients of the eigenfunctions in the boundary regions 1 and n [see Eq. (8)]. The components of the other vectors $\mathbf{c}_i$, $i \neq 1$, are the coefficients of the eigenfunctions in the inner regions [see Eq. (6)]. Notice that once the eigenvalues have been determined, the matrices A_{ij} [Eqs. (13) and (5)] are explicitly determined. We again show that a direct numerical solution of (29) would fail in strongly asymptotic problems, as are most of Quantum Mechanics problems. Let us determine the coefficients of the eigenfunction at the inner region furthest to the right, which is assumed to be outside the turning points in the classically forbidden region. From the last equation of (29), we get

$$\mathbf{c}_{n-1} = -A_{n-1,n-1}^{-1} A_{n-1,1}\mathbf{c}_1 . \tag{31}$$

Consider for the sake of the argument that the eigenfunction is symmetric, then, Table I and [Eq. (8)], we must have

$$B_n = -B_1 = -1, \tag{32}$$

because of the symmetry and also because the eigenfunctions are determined except by a constant factor. Thus,

$$\mathbf{c}_1 = \begin{pmatrix} B_1 \\ B_n \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \end{pmatrix}. \tag{33}$$

After multiplying $A_{n-1,1}$ by $\mathbf{c}_1$ in (31), we get

$$\mathbf{c}_{n-1} = -\begin{pmatrix} \cosh \beta_{n-1}x_{n-1} & -\sinh(\beta_{n-1}x_{n-1})/\beta_{n-1} \\ -\beta_{n-1}\sinh \beta_{n-1}x_{n-1} & \cosh \beta_{n-1}x_{n-1} \end{pmatrix}\begin{pmatrix} \sinh[\beta_n(x_{n-1} - L)]/\beta_n \\ \cosh \beta_n(x_{n-1} - L) \end{pmatrix}. \tag{34}$$

The arguments of the hyperbolic functions in the vector to the right of (34) are $O(1)$, but those in the matrix might be very large, typically in excess of 100. There is no numerical difference then between the hyperbolic sine and the cosine. Performing the matrix multiplication in (34) and using (6), we get for the eigenfunction in region $n - 1$ the following expression

$$y(x) = A(\cosh \beta_{n-1}x - \sinh \beta_{n-1}x) \equiv 0, \tag{35}$$

where A is a certain constant, i.e., for $\beta_{n-1}x > 100$, as there is no numerical difference whatsoever between the two hyperbolic functions; the computation of the eigenfunction would yield zero identically in this region. It is to be stressed that the problem just discussed is a real difficulty, because as there is only one arbitrary constant available, we are forced to start the solution of (29) at the first or at the last equation. This is because in

$$\mathbf{c}_2 = A_{12}^{-1}A_{\ 1}\mathbf{c}_1\,, \qquad \mathbf{c}_{n-1} = -A_{n-1,n-1}^{-1}A_{n-1,1}\mathbf{c}_1\,, \tag{36}$$

the vectors

$$\mathbf{v}_2 = A_{11}\mathbf{c}_1\,, \qquad \mathbf{v}_{n-1} = A_{n-1,1}\mathbf{c}_1 \tag{37}$$

have components which involve only one arbitrary integration constant, B_1 and B_n, respectively [see Eqs. (13) and (30) for the notation of the matrices A and the vectors $\mathbf{c}$]; however, it is impossible to start the integration in an inner equation of (29) because two arbitrary constants are required to define a vector $\mathbf{c}_i$, $i \neq 1$, $n - 1$. Further, if the numerical condition (35) occurs, it will persist in other regions as long as the arguments of the hyperbolic functions remain large; i.e., we would get for the eigenfunction

$$y(x) \equiv 0 \tag{38}$$

identically in part of the domain. Also, the inaccuracies due to this are carried along in the computation of the eigenfunction in the rest of the domain.

This difficulty is solved analytically, just as was done with the eigenvalue Eq. (18), by using the elementary addition formulas for the circular and hyperbolic functions. We now include some elementary algebraic manipulations showing how

this is achieved. If the integration is started in the first equation of (29) (it can be equally stated in the last), we get

$$\begin{aligned} \mathbf{c}_2 &= A_{12}^{-1} A_{11} \mathbf{c}_1 \, ; \\ \mathbf{c}_3 &= A_{23}^{-1} A_{22} A_{12}^{-1} A_{11} \mathbf{c}_1 \, ; \\ \mathbf{c}_4 &= A_{34}^{-1} A_{33} A_{23}^{-1} A_{22} A_{12}^{-1} A_{11} \mathbf{c}_1 \, ; \\ &\cdots \\ \mathbf{c}_m &= A_{m-1,m}^{-1} A_{m-1,m-1} A_{m-2,m-1}^{-1} \cdots A_{11} \mathbf{c}_1 \, . \end{aligned} \tag{39}$$

The last equation of (39), for $m = n - 1$, determines $\mathbf{c}_{n-1}$, and from this and the last equation of (29) we could, in principle, obtain the last integration constant B_n to entirely determine the problem. However, for asymptotic problems with very deep wells, this procedure is not accurate because errors accumulate and propagate if (29) were solved all the way from top to bottom; this is the same as starting with an arbitrary value of the eigenfunction at the left boundary region and integrating all the way to the right boundary. To avoid this difficulty, the solution of (29) as given by (39) is stopped at $m = n/2$, i.e., at the midpoint of the domain, which is always taken at the minimum of the potential function. If the potential were symmetric that is all we need, because the eigenfunctions are symmetric or antisymmetric. For central field problems with asymmetric potentials, after computing the eigenfunctions from the left to the midpoint, (29) is solved starting from the bottom till the midpoint, i.e., the eigenfunction is now computed from the right inward to the midpoint, and then both pieces are matched at the center. It should be noticed that the eigenfunctions so computed are correct except for a factor, i.e., their derivatives match at the midpoint and the matching is achieved by multiplying each piece by its reciprocal value at the center, so that both pieces have also the same midpoint value. Except for the first matrix in the right side of the equations in (39), the others are grouped in pairs, thus,

$$A_{ii} A_{i-1,i}^{-1} = \begin{pmatrix} \cosh \beta_i (x_i - x_{i-1}) & \sinh[\beta_i (x_i - x_{i-1})]/\beta_i \\ \beta_i \sinh \beta_i (x_i - x_{i-1}) & \cosh \beta_i (x_i - x_{i-1}) \end{pmatrix} \tag{40}$$

in the classically forbidden region [see Eqs. (5), (13), and Table I], and

$$A_{ii} A_{i-1,i}^{-1} = \begin{pmatrix} \cos \beta_i (x_i - x_{i-1}) & \sin[\beta_i (x_i - x_{i-1})]/\beta_i \\ -\beta_i \sin \beta_i (x_i - x_{i-1}) & \cos \beta_i (x_i - x_{i-1}) \end{pmatrix} \tag{41}$$

in the allowed region. In this way, the arguments of the hyperbolic functions in (40)

are two orders of magnitude smaller than if the matrices were computed individually. Equations (39) are now written as follows:

$$\begin{aligned} \mathbf{c}_2 &= A_{12}^{-1}\mathbf{v}_2\,, & \mathbf{v}_2 &\equiv A_{11}\mathbf{c}_1\,, \\ \mathbf{c}_3 &= A_{23}^{-1}\mathbf{v}_3\,, & \mathbf{v}_3 &\equiv A_{22}A_{12}^{-1}A_{11}\mathbf{c}_1\,, \\ &\cdots & &\cdots \\ \mathbf{c}_m &= A_{m-1,m}^{-1}\mathbf{v}_m\,, & \mathbf{v}_m &\equiv A_{m-1,m-1}A_{m-2,m-1}^{-1}\cdots A_{11}\mathbf{c}_1\,. \end{aligned} \tag{42}$$

The vectors $\mathbf{v}_i$ in (42) are evaluated grouping the matrices in pairs as shown in (40) and (41), except the last matrix A_{11} where the arguments of the hyperbolic functions are $O(1)$. Also, the vectors $\mathbf{v}_i$ involve only one arbitrary integration constant B_1, see Eqs. (13) and (30). The inverse A matrices at the left in (42) involve still hyperbolic functions with very large arguments, and, therefore, a computation of the coefficients $\mathbf{c}_i$ would present still serious numerical difficulties. However, it is not necessary to compute the coefficients $\mathbf{c}_i$ isolatedly, in order to obtain the eigenfunctions. From Eqs. (6), (30), and (42), we have the following expression for the eigenfunctions in vector notation:

$$y(x) = A_{i-1,i}^{-1}\mathbf{v}_i \cdot \mathbf{f}(\mathbf{x}), \qquad \text{in region} \quad i,\ i \neq 1, n, \tag{43}$$

where $\mathbf{f}(\mathbf{x})$ is the vector function

$$\mathbf{f}(\mathbf{x}) = \begin{pmatrix} F(\beta_i x) \\ G(\beta_i x) \end{pmatrix}. \tag{44}$$

Using Eqs. (13), (42), and (44) and the elementary addition formulas for the circular and hyperbolic functions, the following expression is obtained for the inner product in (43):

$$y(x) = (1/\beta_i)[\beta_i v_{i1} \cosh \beta_i(x_{i-1} - x) - v_{i2} \sinh \beta_i(x_{i-1} - x)] \text{ in region } i \neq 1, n \tag{45}$$

in the classically forbidden region, and

$$y(x) = (1/\beta_i)[\beta_i v_{i1} \cos \beta_i(x_{i-1} - x) - v_{i2} \sin \beta_i(x_{i-1} - x)] \text{ in region } i \neq 1, n \tag{46}$$

in the allowed region. In (45) and (46), the following notation is used

$$\mathbf{v}_i \equiv \begin{pmatrix} v_{i1} \\ v_{i2} \end{pmatrix} \tag{47}$$

for the components of the vectors $\mathbf{v}_i$ defined in (42).

Having been able to use the elementary addition formulas has allowed us to analytically perform the inner product in (43), thus, eliminating the need to evaluate hyperbolic functions with very large arguments. The numerical evaluation of the vectors v in (42) and, therefore, of the eigenfunctions, does not present any numerical problem. It is worth mentioning that once the eigenvalue Eq. (18) has been solved and the eigenvalues stored, the same subroutine *ROOTF* is used to compute the eigenfunctions. This is achieved by substituting the eigenvalue function $f(E) \equiv |A|$ in *ROOTF* by the eigenfunctions $y(x)$, and the range (28) by $0 < x < L$. In this way, the eigenfunctions are computed in the domain and their nodes found automatically.

5. Error Analysis

The method presented in this paper is a first order method, that is, the absolute error both in the eigenvalues and eigenfunctions is $O(h)$, where h is the spatial step size. This can be shown most simply by applying perturbation theory to our approximate problem (1), (2), and (3) (see [10], p. 343). As the potential of the exact differential equation undergoes a perturbation, $O(h)$, when approximated by a step function, a perturbation theory analysis shows that the absolute errors in the eigenvalues and eigenfunctions are also $O(h)$. At first sight, this seems a bad result. However, it must surely represent a conservative upper limit for the absolute errors, because the numerical results to be shown below are at least one order of magnitude better than indicated by the above theoretical error bounds.

6. Numerical Results

In this section we describe some of the results obtained with the computer program that incorporates the method discussed in the previous sections. First, a central field Quantum Mechanics problem was treated, the radial Schrödinger equation (1) with Morse's potential [13],

$$V(x) = D\{1 - \exp[-a(x - x_e)]\}^2 - D, \tag{48}$$

for the following values of the parameters:

$$a = 0.711248, \qquad x_e = 1.9975, \qquad D = 188.4355. \tag{49}$$

The boundary conditions (2) used in conjunction with (47) are

$$y(0) = y(10) = 0. \tag{50}$$

The second problem treated was that of Mathieu's equation [14], where the "potential" is

$$V(x) = 2q \cos 2x, \tag{51}$$

q a positive constant. The boundary conditions (2) are in this case

$$y(0) = y(\pi) = 0. \tag{52}$$

Although Mathieu's equation is not a true Quantum Mechanics problem, it is entirely correct to think of it as if it were so. Indeed, Mathieu's equation, Eqs. (1), (51), and (52), gives the bound states of a particle in a box of length π and infinitely high walls with the potential inside given by (51).

The Schrödinger equation with Morse's potential was chosen because analytic solutions are known [13] and, thus, provide a check for the numerical solutions. Mathieu's equation has been extensively tabulated ([14], [15]), and so accurate numerical data are also available for comparison.

A. Schrodinger Equation with Morse's Potential

We have approximated Morse's potential by a step function with the same number of steps $m = n/2$ in the ranges

$$0 \leqslant x \leqslant 1.9975, \qquad 1.9975 \leqslant x \leqslant 10. \tag{53}$$

The interface is chosen exactly at the abscissa of the minimum of the potential

$$V(1.9975) = V_{\min} = -188.4355. \tag{54}$$

Further, as the potential is more rapidly varying about its minimum than toward the right domain boundary, where it is quite flat, the $n/2$ potential steps in the right range in (53) were taken as follows:

$$n/4 \text{ steps in } 1.9975 \leqslant x \leqslant 4, \qquad \text{and} \qquad n/4 \text{ steps in } 4 \leqslant x \leqslant 10.$$

Explicitly, the approximation is

$$V(x) \approx \begin{cases} V_1 = [V(0) + V(x_1)]/2, & 0 < x < x_1 ; \\ V_2 = [V(x_1) + V(x_2)]/2, & x_1 < x < x_2 ; \\ \quad \cdots & \quad \cdots \\ V_m = -188.4355, & x_{m-1} < x < x_m = 1.9975; \\ V_{m+1} = -188.4355, & x_m < x < x_{m+1} ; \\ V_{m+2} = [V(x_{m+1}) + V(x_{m+2})]/2, & x_{m+1} < x < x_{m+2} ; \\ \quad \cdots & \quad \cdots \\ V_n = [V(x_{n-1}) + V(x_n)]/2, & x_{n-1} < x < x_n = 10; \\ m \equiv n/2, \end{cases} \tag{55}$$

and the three step widths used are thus

$$\begin{aligned} &0 < x < 1.9975, && h_1 = 1.9975/(n/2), \\ &1.9975 < x < 4, && h_2 = (4 - 1.9975)/(n/4) \\ &4 < x < 10, && h_3 = (10 - 4)/(n/4). \end{aligned}$$

The results for the first five eigenvalues, when the potential is approximated by 50, 100, and 200 steps, are given in Table II, together with the analytic results. It

TABLE II

First Five Eigenvalues of Schrödinger Equation with Morse's Potential

n	$-E_0$	$-E_1$	$-E_2$	$-E_3$	$-E_4$
50	178.856	160.219	142.771	126.269	110.772
100	178.795	160.265	142.769	126.281	110.797
200	178.795	160.279	142.776	126.286	110.805
Exact	178.798	160.282	142.780	126.288	110.808

should be noticed that the maximum error in the eigenvalues for $n = 50$ is less than 0.04 percent; for $n = 100$, the maximum error is 0.01 percent; and for $n = 200$, the maximum error is 0.003 percent. The eigenvalues in Table II were obtained by searching for the roots of the eigenvalue Eq. (18) in the range [see (28)]

$$-188.0 \leqslant E \leqslant -108.0. \tag{56}$$

The function $|A| \equiv f(E)$ was evaluated at 20 points in the range (56), and no root was ever missed in the first attempt. We consider this to be the main attraction of the method, that is, the great ease with which any desired number of eigenvalues and eigenfunctions are obtained in one single run of the program, without needing to supply initial guesses for the eigenvalues. Indeed, all that is required is a numerical table of the potential and the search range (28).

B. Mathieu's Equation

In this case, we approximated the "potential" (51) as follows:

$$V(x) = \begin{cases} V_1 = V(0) = 2q, & 0 < x < x_1\,; \\ V_2 = [V(x_1) + V(x_2)]/2, & x_1 < x < x_2\,; \\ \quad \cdots & \quad \cdots \\ V_m = -2q, & x_{m-1} < x < x_m = \pi/2; \\ V_{m+1} = -2q, & x_m < x < x_{m+1}\,; \\ \quad \cdots & \quad \cdots \\ V_n = V(x_n) = 2q, & x_{n-1} < x < x_n = \pi; \\ m \equiv n/2. \end{cases} \tag{57}$$

The potential has the minimum at the center

$$V_{\min} = V(\pi/2) = -2q. \tag{58}$$

It is to be noticed that in both problems, (55) and (57), we have approximated the minimum exactly and also two steps at left and right were set equal to the minimum; this was done for obvious reasons. The results obtained for $q = 40$ are given in Tables III and IV, for $n = 52$, 104, together with the exact results

TABLE III

Eigenvalues of Mathieu's Equation, $q = 40$

n	$-E_0$	$-E_1$	$-E_2$	$-E_3$	$-E_4$
52	67.596	43.316	20.194	−1.7500	−22.335
104	67.599	43.343	20.203	−1.7354	−22.334
Exact	67.606	43.352	20.208	−1.7300	−22.332

TABLE IV

Nodes of Mathieu Eigenfunctions, $q = 40$

n	N_{11}[a]	N_{21}	N_{31}	N_{32}	N_{41}	N_{42}
52	1.57080	1.36624	1.21042	1.57080	1.07562	1.41518
104	1.57080	1.36617	1.21046	1.57080	1.07563	1.41513
Exact	1.57080	1.36616	1.21047	1.57080	1.07565	1.41513

[a] N_{ij} means j-th node of i-th eigenfunction, the index $i = 0$ refers to the fundamental mode, etc.

taken from Ince's papers [15]. It is seen that the accuracy is good with relatively few steps, both for the eigenvalues and the zeros of the eigenfunctions. The case $q = 40$ is a fairly straightforward calculation, because we are not yet in the asymptotic range which is the situation when q is very large. To test the method and the program, we also solved Mathieu's equation for $q = 160$ and $q = 1{,}600$ with free end boundary conditions

$$dy(0)/dx = dy(\pi)/dx = 0.$$

The first three eigenvalues for these cases are given in Table V, together with the

values obtained by S. Goldstein ([14], p. 240). We see that the case $q = 1{,}600$ is truly an asymptotic problem, where [see (27)]

$$E_0 \to V_{\min} = -3{,}200.$$

Here the eigenfunctions are 35 orders of magnitude smaller at the boundaries than at the center, where they cluster. In the limit $q \to \infty$, the nodes of all the eigenfunctions approach asymptotically $\pi/2$, the domain center.

TABLE V

First Three Eigenvalues of Mathieu's Equation for Large Values of the Parameter and Free End Boundary Conditions

	$q = 160$			$q = 1{,}600$		
n	$-E_0$	$-E_1$	$-E_2$	$-E_0$	$-E_1$	$-E_2$
52	294.96	245.22	196.78	3121.6	2960.0	2802.7
104	294.93	245.34	196.82	3120.2	2960.8	2803.0
Accurate[a] value	294.94		196.85	3120.2		2803.3

[a] These "accurate" values were obtained by S. Goldstein and are reported in [14], p. 240. The missing values are not reported.

In order to clearly show the difference between the present method and the more conventional ones, the absolute accuracy of which decreases as the order of the eigenvalues increases, we obtained the first 16 eigenvalues of Mathieu's equation for $q = 100$ and free end boundary conditions. The search range (28) was in this case

$$-181 < E < 250,$$

and the function $|A| \equiv f(E)$ was evaluated at 75 points. The results obtained with 104 steps are given in Table VI, together with the values published in [16]. It is clearly seen that the absolute accuracy is approximately uniform and does not decrease for the higher eigenvalues.

The numerical results obtained confirm the analysis of Section 4, that is, that the method is uniformly valid both for nonasymptotic and asymptotic problems. It should be noticed that all the results reported in Tables II, III, IV, V, and VI, were obtained in one single run of the program, which is written in FORTRAN IV. The calculations were performed on an IBM 360/50 computing system, and the total machine time used was eleven minutes.

TABLE VI

First 16 Eigenvalues of Mathieu's Equation for $q = 100$ and Free End Boundary Conditions

r	E_r Ref. 16	This Work (104 steps)
0	−180.25	−180.24
1	−141.28	−141.25
2	−103.37	−103.35
3	−66.57	−66.55
4	−30.95	−30.94
5	3.43	3.45
6	36.49	36.49
7	68.11	68.12
8	98.15	98.15
9	126.40	126.40
10	152.41	152.41
11	175.07	175.06
12	192.73	192.72
13	207.63	207.63
14	225.77	225.76
15	249.33	249.32

7. Conclusions

The greatest advantages of the method are the simplicity of its application and the fact that it is also valid for strong asymptotic problems. When many different problems need to be solved, the method seems particularly appropriate, because the solutions can be obtained very easily knowing only the range where the eigenvalues are, and this range is given analytically by (28). The greatest need for improvement lies in the area of error analysis, a question we have not explored fully. It is only known for certain that more steps in the potential result in more accurate solutions, because the approximate problem solved approaches asymptotically the exact problem for an infinitesimally small step width. Thus, the number of steps in the potential can be increased till the results obtained become stationary at the desired accuracy. However, it would be very important to know what is the "best" step function for a given number of steps that results in the most accurate solution to the problem. In our calculations, we found that the fundamental eigenvalue specially and the higher eigenvalues to a lesser degree are quite sensitive to the way in which the potential is approximated near its minimum, while relatively insensitive to the approximation chosen away from the minimum. This is specially true in problems with very deep wells.

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