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Eigenvalues of the Schrödinger equation via the Riccati-Padé method

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A method described previously for obtaining upper and lower bounds for the eigenenergies of the Schrödinger equation for parity-invariant and central potentials is extended and applied to asymmetric one-dimensional potentials. The procedure consists of transforming the Schrödinger equation into a Ricati one for the logarithmic derivative of the wave function. The solution of the latter equation is approached by a series of Padé approximants. Approximate eigenenergies are obtained from the roots of associated determinants, and such roots are proved, in some cases, to be upper or lower bounds to the actual eigenenergies. The method is illustrated by calculations for several model potentials and the results compared with those obtained by alternative procedures.

I. INTRODUCTION

Recently, a method has been presented for obtaining upper and lower bounds to the eigenvalues of the Schrödinger equation.[1,2] It consists of transforming the Schrödinger equation into a Riccati one and approaching the solution of the latter by means of a sequence of Padé approximants. The bounds are obtained from the roots of a sequence of related determinants. The method has been successfully applied to several one-dimensional and central-field problems,[1] and a proof for the occurrence of bounds has been proposed for the case of polynomial potentials.[2] However, a more careful investigation shows that such a proof is limited to polynomials of degree less than or equal to 4.

The purpose of the present paper is to discuss the Riccati-Padé method in more detail and to give a more complete explanation for the occurrence of bounds. In addition to this, the method is applied to one-dimensional asymmetric potentials which have not been treated before in this way. The paper is organized as follows: the main equations are developed in Sec. II for parity-invariant potentials, and results are shown for the harmonic oscillator as an introductory example. A proof of the bounds is presented in Sec. III for the case of parity-invariant, one-dimensional, and central-field potentials. Asymmetric potentials are discussed in Sec. IV. In every case, the analytical conclusions have been verified by means of symbolic algebraic (REDUCE) calculations.

II. PARITY-INVARIANT POTENTIALS

To begin with, we consider the time-independent Schrödinger equation

$$\psi(x)''=[V(x)-E]\psi(x)\ , \tag{1}$$

where $V(x)=V(-x)$. It is convenient to define a new function $\Phi(x)=x^{-s}\psi(x)$, where $s=0$ or $s=1$ for even or odd states, respectively. In this way, the logarithmic derivative

$$f(x)\equiv[-\Phi(x)]'/\Phi(x) \tag{2}$$

is regular at the origin for all eigenstates of (1). It follows from Eqs. (1) and (2) that $f(x)$ satisfies the Riccati equation

$$[f(x)]'-f(x)^2+2sf(x)/x=E-V(x)\ . \tag{3}$$

Although the Riccati-Padé method applies to quite general potentials $V(x)$,[1] in this section we restrict ourselves to the simple forms:

$$V(x)=\sum_{j=1}^{K} v_j x^{2j},\quad v_K>0\ . \tag{4}$$

The logarithmic derivative (2) can be expanded in a Taylor series around the origin

$$f(x)=\sum_{j=0}^{\infty} f_j x^{2j+1}\ , \tag{5}$$

where the coefficients f_j are found to satisfy

$$f_j=(2j+2s+1)^{-1}\left[\sum_{i=0}^{j-1} f_i f_{j-i-1}+E\delta_{j0}-\sum_{i=1}^{K} v_i\delta_{ij}\right] . \tag{6}$$

The function $f(x)$ can be approximated by a sequence of rational functions

$$g(x)=A(x)/B(x) , \tag{7}$$

where

$$A(x)=\sum_{j=0}^{M} a_j x^{2j+1},\quad B(x)=\sum_{j=0}^{N} b_j x^{2j},\quad b_0=1 . \tag{8}$$

If $g(x)$ is exactly a Padé approximant, then $f(x)-g(x)=O(x^{2(M+N)+3})$. However, since the energy eigenvalue E is unknown, we can consider it as an adjustable parameter and obtain an approximation to it according to the following procedure. It seems reasonable to choose the energy such that $f(x)-g(x)=O(x^{2(M+N)+5})$ because, in this way, $g(x)$ approaches the solution of the Riccati equation more accurately around $x=0$. Under such conditions, the coefficients a_j and b_j satisfy

$$\sum_{i=0}^{j} b_i f_{j-i}=a_j,\quad j=0,1,\ldots,M , \tag{9a}$$

$$\sum_{i=0}^{j} b_i f_{j-i}=0,\quad j=M+1,M+2,\ldots,M+N+1 , \tag{9b}$$

where it is understood that $b_i=0$ if $i>N$. The N coefficients $b_1,b_2,\ldots,b_N$ cannot satisfy the $N+1$ linear, homogeneous equations (9b) unless

$$H_D^d=\begin{vmatrix} f_{d+1} & f_{d+2} & \cdots & f_{d+D}\\ f_{d+2} & f_{d+3} & & f_{d+D+1}\\ \vdots & & \ddots & \vdots\\ f_{d+D} & f_{d+D+1} & \cdots & f_{d+2D-1}\end{vmatrix}=0 , \tag{10}$$

where $d=M-N\geq 0$ and $D=N+1$. It has been found previously[1] that the roots W of the $D\times D$ determinant (10) converge very quickly towards the actual eigenenergies E as D increases, thus yielding increasingly tight upper and lower bounds.[1,2] Such behavior has been verified for several potential models[1] although it is not clear why or if the bounds occur in general. The proof that has been proposed[2] only applies when $K\leq 2$ as shown in Sec. III.

It is instructive to show first how the method applies to the harmonic oscillator ($v_i=\delta_{i1}$) because in this case all the eigenvalues are exactly obtained. The first few determinants for the even parity states are

$$H_2^0=(E^2-1)^2(E^2-25)/4725 , \tag{11a}$$

$$H_2^1=(E^2-1)^2(E^2-25)(E^2+3)/297\,675 , \tag{11b}$$

$$H_3^0=(E^2-1)^3(E^2-25)^2(E^2-81)/46\,414\,974\,375 , \tag{11c}$$

etc. These results suggest that $H_D^d=(E^2-1)^D(E^2-5^2)^{D-1}\cdots[E^2-(4D-3)^2]P_D^d(E)$, where $P_D^d(E)$ is a polynomial with no real roots. The fact that the degeneracy of each root increases with the order of the determinant has an important consequence when nonexactly solvable problems are treated. In such cases, it is found that the number of roots in the neighborhood of a given eigenvalue increases as D increases. In practice, this problem can be overcome by looking for nested pairs of upper and lower bounds[1,2] as one increases the value of D.

III. UPPER AND LOWER BOUNDS

The existence of upper and lower bounds can be rigorously proved in some cases. To this end, we follow the procedure proposed in Ref. 2 and define the ansatz for the Schrödinger equation

$$G(x)-x^s\exp[-\int^x g(x')dx'] , \tag{12}$$

where $g(x)$ is given by Eq. (7); V_g is the corresponding potential

$$V_g(x)=W+G(x)''/G(x)\equiv V(x)+R(x) , \tag{13}$$

where $R(x)$ is determined below. Therefore, it is clear from the Schrödinger equation that if $R(x)>0$ for all x, then $W>E$. On the other hand, if $R(x)<0$ for all x, then $HG(x)/G(x)=W-R(x)\geq W$, where H is the Hamiltonian operator. It follows from theorems 3 and 4 in Ref. 3 that $W\leq\inf[HG(x)/G(x),G(x)]\leq E$. One of the main advantages of the Riccati-Padé method is that it leads to simple functions $R(x)$ as shown now. It follows from Eqs. (7), (12), and (13) that

$$R(x)B(x)^2=A(x)^2-A(x)'B(x)-A(x)B(x)' \\ -2sA(x)B(x)/x+[W-V(x)]B(x)^2 . \tag{14}$$

Therefore

$$R(x)B(x)^2=\sum_{j=0}^{J} r_j x^{2j} , \tag{15}$$

where

$$J=\max(2M+1,2N+K) , \tag{16}$$

because $M\geq N$ as stated above. Since the coefficients a_j and b_j, and the approximate eigenvalues W have been chosen so that $g(x)$ satisfies the Riccati equation as accurately as possible around the origin, we conclude that

$$r_j=0,\quad j=0,1,\ldots,M+N+1 . \tag{17}$$

In other words, the $M+N+2$ parameters a_i, $i=0,1,\ldots M$, b_j, $j=1,2,\ldots,N$, and W have been chosen in order to satisfy Eq. (17). This procedure is closely related to the τ method,[4] except that in the present case, the eigenvalue is also considered to be an adjustable parameter. As a result, the function $R(x)$ can be written in the form

$$R(x)=\sum_{j=I}^{J} r_j x^{2j}/B(x)^2,\quad I=M+N+2 . \tag{18}$$

If $2M+1\geq 2N+K$, then $J=2M+1$ and $J-I$

$\geq (K-3)/2$. On the other hand, if $2M+1<2N+K$, it is found that $J-I>(K-3)/2$. Therefore $R(x)$ can be reduced to only one term provided that $K\leq 3$. When $K=2$ (quartic oscillator), it is found that

$$R(x) = -v_2 b_N^2 x^{4N+4}/B(x)^2, \quad M=N \tag{19}$$

and

$$R(x) = a_M^2 x^{4M+2}/B(x)^2, \quad M=N+1 \ . \tag{20}$$

For this reason, the roots of the determinants H_D^0 and H_D^1 yield lower and upper bounds, respectively.[1,2] When $K=3$ (sextic oscillator), it can be easily proved that $R(x)$ has only one term provided that $M=N+1$, in which case

$$R(x) = (a_M^2 - v_3 b_N^2) x^{4M+2}/B(x)^2 \ . \tag{21}$$

Therefore, $W>E$ ($W<E$) when $a_M^2 > v_3 b_N^2$ ($a_M^2 < v_3 b_N^2$). Explicit numerical results for the sextic oscillator are discussed in Ref. 1.

The analysis becomes more difficult as K increases. For instance, when $K=4$ (octic oscillator), it is found that

$$R(x) = -(v_4 b_N^2 x^2 + v_3 b_N^2 + 2v_4 b_N b_{N-1} - a_{N+1}^2)/B(x)^2 \tag{22}$$

when $M=N+1$, and

$$R(x) = (a_{N+2}^2 x^2 + 2a_{N+2}a_{N+1} - v_4 b_N^2) x^{4N+8}/B(x)^2 \ , \tag{23}$$

when $M=N+2$. Other choices of M and N lead to more complex functions $R(x)$ and, therefore, we discuss here only the bounds obtained from (22) and (23). When arguing as before, we conclude that $W-R_m<E$ in the former case and that $W-R_m>E$ in the latter one, where $R_m=\max_{\{x\}}[R(x)]>0$ and $R_m=\min_{\{x\}}[R(x)]<0$, respectively. Results are shown in Table I for the ground state of the octic oscillator $V(x)=x^8$. As can be seen from Table I, the roots of the determinants H_D^d converge quickly toward the actual eigenvalues[5] as D increases. A quite unexpected result is the absence of roots of H_5^2 for the ground state, and the same situation is found in the case of the first excited state as shown in Table II. In some cases, the form of R_m does not allow us to draw any definite conclusions concerning the nature of the roots; these are indicated by dashed lines in Table I. In other cases, especially for the low-order determinants, the corrections R_m are so large that the bounds are meaningless (e.g., H_3^2 and H_5^1 in Table I), although in others, R_m is very small (e.g., H_6^2) and tight bounds can be determined. Notwithstanding the problem of determining bounds, in all cases (except H_5^2 as noted above), the roots themselves yield good approximations to the actual ground-state eigenvalues. Another type of difficulty is encountered when one attempts to determine the higher-state eigenvalues, especially from low-order determinants; viz., the Newton-Raphson method employed to find the roots is unstable and, independent of the initial guess, the method converges to a lower-order eigenenergy. These cases are indicated in Table II by dashed lines. No attempt was made in the present study to improve the search routine because this problem can easily be circumvented by considering higher-order determinants.

The conclusions drawn above for one-dimensional parity-invariant potentials also apply to central-field models with potentials of the form

$$V(r) = -\frac{z}{r} + \sum_{j=1}^{L} v_j r^j \tag{24}$$

because the Riccati equation for both problems is similar.[1] Upper and lower bounds have also been found in the case of nonpolynomial potentials such as the Yukawa potential.[1] However, the theoretical proof of such bounds has not been rigorously given.

IV. ASYMMETRIC POTENTIALS

We now consider the Schrödinger equation (1) where

$$V(x) = \sum_{j=2}^{2K} v_j x^j, \quad v_{2K}>0 \ . \tag{25}$$

TABLE I. Upper bounds (UB) and lower bounds (LB) to the ground state of the octic oscillator $V(x)=x^8$.

	W	R_m	$W-R_m$	Type of bound
H_3^1	1.227 705 428 6	0.316 749 191 4	0.910 956 327 2	LB
H_3^2	1.216 262 341 2	−11 915	11 916	UB
H_4^0	1.219 052 323 5	- - -	- - -	- - -
H_4^1	1.223 672 404 3	0	1.223 672 404 3	LB
H_4^2	1.226 062 376 9	0	1.226 062 376 9	UB
H_5^0	1.226 659 815 4	- - -	- - -	- - -
H_5^1	1.225 917 075 3	211 672	−211 671	LB
H_5^2	See text			
H_6^0	1.225 667 863 6	- - -	- - -	- - -
H_6^1	1.225 807 078 5	0	1.225 807 078 5	LB
H_6^2	1.225 820 117 6	−0.000 017 464 0	1.225 837 581 6	UB
Exact[a]	1.225 820 113 8			

[a]Reference 5.

TABLE II. Roots of H_D^d for the first few excited states of the octic oscillator $V(x)=x^8$.

	W		
	First excited state	Second excited state	Third excited state
H_3^1	4.763 829 353 2	---	---
H_3^2	4.721 128 224 2	10.668 558	---
H_4^0	4.731 511 903 8	---	---
H_4^1	4.748 297 378 9	10.292 610	17.547 572 984
H_4^2	4.756 715 104 4	10.093 381	16.404 143 995
H_5^0	4.758 829 269 6	10.166 598	17.108 356 368
H_5^1	4.756 230 356 6	10.224 287	17.288 621 094
H_5^2	See text	10.246 916	17.346 810 762
H_6^0	4.755 324 415 7	10.253 533	17.366 467 188
H_6^1	4.755 828 862 7	10.246 266	17.347 684 170
H_6^2	4.755 874 115 4	10.247 179	17.346 897 995
Exact[a]	4.755 874 410 40	10.244 946 977 2	

[a]Reference 5.

The Riccati equation for

$$f(x)=[-\psi(x)]'/\psi(x) \tag{26}$$

is

$$[f(x)]'=f(x)^2+E-V(x) . \tag{27}$$

Since $f(x)$ is regular at the origin, it can be expanded in a Taylor series

$$f(x)=\sum_{j=0}^{\infty} f_j x^j \tag{28}$$

where

$$f_{n+1}=(n+1)^{-1}\left[\sum_{j=0}^{n} f_j f_{n-j}-\sum_{j=2}^{2K} v_j\delta_{jn}+E\delta_{n0}\right] . \tag{29}$$

In this case, both E and $f_0=[-\psi(0)]'/\psi(0)$ are unknown and treated as adjustable parameters. The approximate solution to the Riccati equation (27) can be written as in Eq. (7) where

$$A(x)=\sum_{j=0}^{M} a_j x^j, \quad B(x)=\sum_{j=0}^{N} b_j x^j . \tag{30}$$

Since in this case there is an additional adjustable parameter f_0, we require that $f(x)-g(x)=O(x^{M+N+3})$, which leads to the conditions

$$\sum_{j=0}^{M} b_j f_{m-j}=a_m, \quad m=0,1,\ldots,M \tag{31a}$$

and

$$\sum_{j=0}^{m} b_j f_{m-j}=0, \quad m=M+1,M+2,\ldots,M+N+2 \tag{31b}$$

where, as before, $b_j=0$ if $j>N$. If the N unknowns b_j, $j=1,2,\ldots,N$ are to satisfy the $N+2$ homogeneous linear equations (31b), it is required that

$$H_D^d=H_D^{d+1}=0 , \tag{32}$$

where $D=N+1$ and $d=M-N\geq 0$. These two equations determine E and f_0 approximately. As in the case of the parity-invariant potentials, we define the approximate potential $V_g(x)=V(x)+R(x)$. A straightforward calculation shows that in the present case we can write

$$R(x)B(x)^2=\sum_{j=I}^{J} r_j x^j , \tag{33a}$$

where

$$I=M+N+2, \quad J=\max(2M,2N+2K) . \tag{33b}$$

When $M\geq N+K$, it follows that $J-I\geq K-2$. Therefore, the simplest nontrivial case is $K=2$, and we will discuss this in what follows. When $M=N+2$, $R(x)$ reduces to just one term,

$$R(x)=(a_{N+2}^2-v_2 b_N^2)x^{2N+4}/B(x)^2 , \tag{34}$$

and the arguments in Sec. III enable us to conclude that $W<E$ ($W>E$) if $a_{N+2}^2>v_2 b_N^2$ ($a_{N+2}^2<v_2 b_N^2$), where W is a root of the determinants in Eq. (32).

As a specific example, we consider the Hamiltonian

$$H=-\tfrac{1}{2}d^2/dx^2+x^2+0.01(x^3+x^4) , \tag{35}$$

and upper and lower bounds to the lowest eigenenergy are compared in Table III with results obtained by other methods.[6] Similar results are obtained for other choices of the anharmonicity coefficients.[6]

Before concluding, there are several points which we

TABLE III. Upper and lower bounds to the lowest eigenvalue of the Hamiltonian (35) obtained from the roots of $H_D^2=H_D^3=0$.

D	W	f_0
3	0.528 025 67	0.007 203 16
4	0.506 952 452	0.009 765 128 8
Exact[a]	0.507 136 887	

[a]Reference 6.

would like to emphasize. First, the use of a rational function approximation to $g(x)$, in contradistinction to a power series,[7] is necessary in order to ensure convergence of the approximate eigenenergies. Second, the accuracy of both the eigenenergies and the corresponding bounds can be improved by considering higher-order determinants. Finally, to avoid algebraic or round-off errors, all results shown in this paper are accurate up to the last digit because the calculations have been carried out by means of the algebraic program REDUCE.

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