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### Tight upper and lower bounds for energy eigenvalues of the Schrödinger equation

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A method is presented for the calculation of tight upper and lower bounds for the energy eigenvalues of the Schrödinger equation. The method is based on a rational functional approximation for the series expansion of the solution of the Riccati equation for the logarithmic derivative of the wave function. Specific applications for one-dimensional anharmonic oscillators and for the Yukawa potential are given, and the present results are compared with those obtainable by other procedures.

#### I. INTRODUCTION

The Riccati equation satisfied by the logarithmic derivative of the wave function proves to be useful in obtaining the eigenenergies of the Schrödinger equation. This can be accomplished either through perturbation theory<sup>1</sup> or by truncating the Taylor series for the logarithmic derivative of the wave function.<sup>2,3</sup> Although the latter procedure, which only applies to nodeless eigenfunctions, yields acceptable results, it is found to be divergent.<sup>3</sup> For this reason, Fernández, Frydman, and Castro<sup>4</sup> proposed a rational functional approximation for the Taylor series which gives rapidly converging upper and lower bounds to the eigenenergies.

The purpose of the present paper is to generalize and improve the method developed by Fernández *et al.*,<sup>4</sup> and to apply it to some specific model potentials of physical interest. The generalized method is discussed in Sec. II. It is applied in Sec. III to two one-dimensional anharmonic oscillators and in Sec. IV to the Yukawa potential. The resulting bounded eigenenergies are compared with those obtained by other workers using various alternative theoretical approaches.<sup>5,6</sup> Discussion and conclusions concerning the method are presented in Sec. V.

#### II. THE METHOD

The present procedure applies to one-dimensional parity-invariant model potentials [i.e.,  $V(-x)=V(x)$ ] and to central force problems [i.e.,  $V(\mathbf{r})=V(r)$ ]. To illustrate it, we first consider the Schrödinger eigenvalue equation in the one-dimensional case,

$$H\Psi = E\Psi, \quad H = -d^2/dx^2 + V(x). \quad (1)$$

We define  $\Phi(x)$  as follows:

$$\Phi(x) = x^{-s}\Psi(x), \quad (2)$$

where  $s=0$  or  $s=1$  for the even or odd states, respectively. Since  $\Phi(0) \neq 0$ , the logarithmic derivative

$$f(x) \equiv -\Phi(x)'/\Phi(x) \quad (3)$$

will be analytic at the origin and can be expanded in a Taylor series,

$$f(x) = \sum_{j=0}^{\infty} f_j x^{2j+1}. \quad (4)$$

Upon substituting Eqs. (2) and (3) into (1), it is found that  $f(x)$  obeys the Riccati equation

$$f(x)' - f(x)^2 + 2sf(x)/x = E - V(x), \quad (5)$$

where  $f(x)' \equiv df(x)/dx$ . If  $V(x)$  is expanded in the series

$$V(x) = \sum_{j=0}^{\infty} v_j x^{2j}, \quad (6)$$

then it follows from Eqs. (4)–(6) that

$$f_j = (2j + 2s + 1)^{-1} \left[ \sum_{i=0}^{j-1} f_i f_{j-i-1} + E\delta_{j0} - v_j \right], \quad j=0, 1, \dots \quad (7)$$

As shown previously,<sup>4</sup> the logarithmic derivative  $f(x)$

can be approximated by a rational function

$$g(x) = A(x)/B(x), \tag{8}$$

where

$$A(x) = \sum_{j=0}^M a_j x^{2j+1}, \quad B(x) = \sum_{j=0}^N b_j x^{2j}, \quad b_0 = 1. \tag{9}$$

Thus, there are  $M + N + 2$  adjustable parameters in the approximated function  $g(x)$ , namely, the coefficients  $a_j$  and  $b_j$  and the energy. From now on,  $W$  and  $E$  will stand for the approximate and exact eigenenergies, respectively. According to Eq. (7),  $f_j$  will be a polynomial in  $E$  (or  $W$ ) of degree  $j + 1$ . For instance,  $f_0 = (W - v_0)/(2s + 1)$ ,  $f_1 = [(W - v_0)^2 - v_1(2s + 1)^2]/[(2s + 1)^2(2s + 3)]$ , etc. If the coefficients  $a_j$  and  $b_j$  and  $W$  are chosen such that

$$g(x) = \sum_{j=0}^{M+N+1} f_j(W)x^{2j+1} + O(x^{2(M+N)+5}), \tag{10}$$

then it follows that

$$\sum_{i=0}^n b_i f_{n-i} = a_n, \quad n = 0, 1, \dots, M \tag{11a}$$

and

$$\sum_{i=0}^n b_i f_{n-i} = 0, \quad n = M + 1, M + 2, \dots, M + N + 1, \tag{11b}$$

where it is understood that  $b_i = 0$  if  $i > N$ . The  $N$  coefficients  $b_1, b_2, \dots, b_N$  cannot satisfy the  $N + 1$  linear homogeneous equations (11b) unless

$$H_D^d \equiv \begin{vmatrix} f_{d+1} & f_{d+2} & \cdots & f_{d+D} \\ f_{d+2} & f_{d+3} & \cdots & f_{d+D+1} \\ \dots & \dots & \dots & \dots \\ f_{d+D} & f_{d+D+1} & \cdots & f_{d+2D-1} \end{vmatrix} = 0, \tag{12}$$

where  $d = M - N \geq 0$  and  $D = N + 1$ . The roots of the  $D \times D$  determinant  $H_D^d, W$ , converge towards the actual eigenenergies  $E$  as  $D$  increases in a manner that provides increasingly accurate upper and lower bounds. This behavior, as verified computationally for a number of potentials, is a marked improvement over the method discussed in Ref. 3 which diverges with increasing  $N$  after

TABLE I. Numerical results for the energy eigenvalues of the quartic oscillator, Eq. (18), illustrating the rapidly converging upper and lower bounds. The best values are underlined.

$D$	$H_D^0$	$H_D^1$	$H_D^2$
Ground state			
3	1.060 234 46	1.060 376 07	1.060 359 63
4	1.060 360 57	1.060 362 26	1.060 362 07
5	1.060 362 07	1.060 362 092 3	1.060 362 090 32
6	1.060 362 090 290 1	1.060 362 090 504 7	1.060 362 090 481
7	1.060 362 090 482 0	<u>1.060 362 090 484 5</u>	<u>1.060 362 090 484 15</u>
"Exact" <sup>a</sup>	1.060 362 090 484 18		
First excited state			
3	3.799 287 93	3.799 714 71	3.799 665 90
4	3.799 668 55	3.799 673 50	3.799 672 96
5	3.799 672 97	3.799 673 03	3.799 673 029 05
6	3.799 673 029 238	3.799 673 029 860	3.799 673 029 793
7	3.799 673 029 7952	<u>3.799 673 029 802</u>	<u>3.799 673 029 801 31</u>
"Exact" <sup>a</sup>	3.799 673 029 80139		
Second excited state			
3	7.3615	7.4659	7.4535
4	7.454 596 86	7.455 816 13	7.455 678 02
5	7.455 685 33	7.455 699 28	7.455 697 74
6	7.455 697 79	7.455 697 953	7.455 697 935 9
7	7.455 697 936 4	<u>7.455 697 938 2</u>	<u>7.455 697 937 97</u>
"Exact" <sup>a</sup>	7.455 697 937 986 7		
Third excited state			
3	11.3757	11.6726	11.6389
4	11.641 737 6	11.645 066 2	11.644 692 0
5	11.644 711 4	11.644 749 2	11.644 744 9
6	11.644 745 1	11.644 745 52	11.644 745 506
7	11.644 745 507 2	<u>11.644 745 512</u>	<u>11.644 745 511 32</u>
"Exact" <sup>a</sup>	11.644 745 511 378		

<sup>a</sup>Reference 5.

TABLE II. Numerical results for the energy eigenvalues of the sextic oscillator, Eq. (19), illustrating the rapidly converging upper and lower bounds. The best values are underlined.

$D$	$H_D^0$	$H_D^1$	$H_D^2$
Ground state			
3	1.136 053	1.144 196	1.145 159
4	1.145 233	1.144 522	1.144 789
5	1.144 790 2	1.144 801 80	1.144 802 85
6	1.144 802 86	<u>1.144 802 475</u>	<u>1.144 802 441</u>
“Exact” <sup>a</sup>	1.144 802 453 7		
First excited state			
4	4.340 065	4.338 668	4.297 389
5	4.338 557	4.338 596	4.338 600 0
6	4.338 600	<u>4.388 598 78</u>	<u>4.338 598 67</u>
“Exact” <sup>a</sup>	4.338 598 711		
Second excited state			
4	8.9806	9.0661	9.0769
5	9.0780	9.073 31	9.072 94
6	9.072 95	<u>9.073 077</u>	<u>9.073 089</u>
“Exact” <sup>a</sup>	9.073 084 56		
Third excited state			
4	14.6625	14.9132	14.9468
5	14.9509	14.9359	14.9347
6	14.9348	<u>14.935 147</u>	<u>14.935 183</u>
“Exact” <sup>a</sup>	14.935 169		

<sup>a</sup>Reference 5.

reaching a “best” value.

As mentioned above, the present method also applies to central force problems. In this case, the radial part of the Schrödinger equation

$$\Psi(r)'' + \frac{2}{r}\Psi(r)' + \{2[E - V(r)] - l(l+1)/r^2\}\Psi(r) = 0 \quad (13)$$

can be transformed into the Riccati equation

$$f(r)' = f^2(r) - \frac{2(l+1)}{r}f(r) + 2[E - V(r)], \quad (14)$$

where  $f(r) = -\Phi(r)'/\Phi(r)$  and  $\Phi(r) = r^{-l}\Psi(r)$ . Therefore, if we again expand the potential in a series

$$V(r) = \sum_{j=-1}^{\infty} v_j r^j, \quad (15)$$

we can write

$$f(r) = \sum_{j=0}^{\infty} f_j r^j, \quad (16)$$

where

$$f_0 = -v_{-1}/(l+1) \quad (17a)$$

and

$$f_{j+1} = (2l+j+3)^{-1} \left[ \sum_{i=0}^j f_i f_{j-i} - 2v_j + 2E\delta_{j0} \right], \quad j=0, 1, \dots \quad (17b)$$

On reasoning as before, it is found that the approximate eigenenergies are also given by the roots of  $H_D^d$ .

Since the rational functional form (Padé approximant) can take into account the poles of  $f(x)$  which occur naturally for simple potentials [e.g.,  $V(x) = x^2$ ], the method developed above applies to all the states, not only to the nodeless ones. Other methods, e.g., the moment method proposed by Handy and Bessis,<sup>7</sup> need special adaptations in order to treat excited states. If  $E_0 < E_1 < \dots$ , then it is found that  $H_2^d$  provides the first approximation to  $E_s$ ;  $H_3^d$  yields the second approximation to  $E_s$  and the first one to  $E_{s+2}$ , etc. In general, the roots of  $H_D^d$  are the  $(D-j-1)$ th approximation to  $E_{s+2j}$ ,  $j=0, 1, \dots, D-2$ . Numerical investigation suggests that the zeros of  $H_D^d$  provide rapidly converging upper and lower bounds to the eigenenergies of the Schrödinger equation as the order of the determinant increases. Unfortunately, we are not at present able to provide a rigorous proof for this behavior. However, we can numerically verify these conclusions if accurate eigenenergies exist for some particular potentials.

In order to eliminate errors, we have employed the

TABLE III. Numerical results for the ground-state energy eigenvalues of the Yukawa potential, Eq. (20), for the choice  $\lambda=0.1$ . The best values are underlined.

$D$	$H_D^0$	$H_D^1$	$H_D^2$
3	-0.407 058 021 9	-0.407 060 960 2	-0.407 058 030 59
4	-0.407 058 030 620 0	-0.407 058 030 613	-0.407 058 030 841
5	-0.407 058 030 613 404 1	-0.407 058 030 613 402 4	-0.407 058 030 613 403 1
6	-0.407 058 030 613 402 9	<u>-0.407 058 030 613 403 17</u>	<u>-0.407 058 030 613 403 158</u>

algebraic program REDUCE wherever possible for algebraic manipulations, and have carried out the numerical calculations in REDUCE keeping a large number of digits (typically 80). Thus the numerical results reported are not affected by round-off errors. This is particularly important in the present method because of the large cancellations that occur in the evaluation of determinants.

### III. ONE-DIMENSIONAL ANHARMONIC OSCILLATORS

As specific applications of the theoretical expressions discussed in Sec. II, we first consider the quartic oscillator

$$V(x) = x^4 \quad (18)$$

which is a particular case of Eq. (6) having  $v_j = \delta_{j2}$ . Re-

sults for the lowest four eigenenergies for several choices of  $d$  and  $D$  are listed in Table I. It is clear from these results that  $H_D^0$  and  $H_D^2$  yield increasing lower bounds while  $H_D^1$  yields a decreasing upper bound as the order  $D$  increases. For  $D$  as small as 7, the agreement of the best bounds (underlined in Table I) with the accurate numerical eigenvalues reported previously by other authors<sup>5</sup> is remarkable.

In the case of the sextic oscillator,

$$V(x) = x^6, \quad (19)$$

having  $v_j = \delta_{j3}$ , the roots of  $H_D^d$  oscillate as the order  $D$  increases giving alternating upper and lower bounds as illustrated by the results listed in Table II. The best bounds, which are underlined, again agree very well with the previous accurate numerical calculations.<sup>5</sup> We would

TABLE IV. Upper and lower bounds for various values of the range  $\lambda$  for the 1s and 2s states of the Yukawa potential, Eq. (20). The best values are underlined.

1s state	
$\lambda=0.1$	
$E(H_6^0) = -0.407\ 058\ 030\ 613\ 404\ 1$	$< E < E(H_6^0) = -0.407\ 058\ 030\ 613\ 402\ 9$
$E(H_6^1) = -0.407\ 058\ 030\ 613\ 403\ 17$	$< E < E(H_6^1) = -0.407\ 058\ 030\ 613\ 402\ 4$
$E(H_6^2) = \underline{-0.407\ 058\ 030\ 613\ 403\ 158}$	$< E < E(H_6^2) = \underline{-0.407\ 058\ 030\ 613\ 403\ 135}$
"Exact" <sup>a</sup> $E = -0.407\ 058\ 030\ 613\ 403\ 156\ 7$	
$\lambda=0.2$	
$E(H_6^0) = -0.326\ 808\ 511\ 4$	$< E < E(H_6^0) = -0.326\ 808\ 492\ 8$
$E(H_6^1) = -0.326\ 808\ 511\ 369\ 699$	$< E < E(H_6^1) = -0.326\ 808\ 511\ 369\ 08$
$E(H_6^2) = \underline{-0.326\ 808\ 511\ 369\ 203}$	$< E < E(H_6^2) = \underline{-0.326\ 808\ 511\ 368\ 75}$
"Exact" <sup>a</sup> $E = -0.326\ 808\ 511\ 369\ 193$	
$\lambda=0.5$	
$E(H_6^0) = -0.148\ 117\ 043$	$< E < E(H_6^0) = -0.148\ 117\ 020$
$E(H_6^1) = \underline{-0.148\ 117\ 022\ 2}$	$< E < E(H_6^1) = -0.148\ 117\ 008$
$E(H_6^2) = -0.148\ 117\ 032\ 3$	$< E < E(H_6^2) = \underline{-0.148\ 117\ 021\ 5}$
"Exact" <sup>a</sup> $E = -0.148\ 117\ 021\ 89$	
2s state	
$\lambda=0.2$	
$E(H_5^0) = -0.012\ 175$	$< E < E(H_5^0) = -0.012\ 100$
$E(H_5^1) = -0.012\ 267$	$< E < E(H_5^1) = -0.012\ 11$
$E(H_5^2) = \underline{-0.012\ 143}$	$< E < E(H_5^2) = \underline{-0.012\ 107\ 11}$
"Exact" <sup>a</sup> $E = -0.012\ 107\ 86$	

<sup>a</sup>Reference 6.

expect similar behavior in other parity-invariant potentials, and work is in progress to extend the method to include other (e.g., odd powers) potentials.

#### IV. CENTRAL POTENTIALS

As an application of the present method to a central force problem, we consider the Yukawa potential

$$V(r) = -\frac{1}{r} e^{-\lambda r}, \quad (20)$$

where the range  $\lambda$  can be chosen arbitrarily. For the ground ( $1s$ ) state and the choice  $\lambda = 0.1$ , we obtain the results listed in Table III. Similar results obtain for other choices of  $\lambda$  and for other states. These are illustrated by sample results presented in Table IV. We give only the results for  $D \leq 7$  for several choices of  $\lambda$  for the  $1s$  and  $2s$  states. As can be seen from these results, the convergence for the eigenenergies of the Yukawa potential is extremely rapid. This is especially true for small values of  $\lambda$  for which the Yukawa potential becomes more Coulombic in nature. This behavior could be anticipated because in the limit  $\lambda \equiv 0$  (hydrogenic atoms), it is well known that the logarithmic derivative  $f(r)$  can be exactly represented as a Padé approximant.

#### V. DISCUSSION AND CONCLUSIONS

As one can see from the results presented in Tables I–IV, the method described in Sec. II gives accurate upper and lower bounds for both parity-invariant and

central potentials. These bounds can, in principle, be made increasingly more accurate by increasing the order of the determinants  $H_D^d$ , although numerical stability problems may occur if one attempts to use high-order determinants. In practice, however, even small determinants, say,  $6 \times 6$ , give reasonable accuracy for the potentials considered. Also, for the one-dimensional case, the nature of the bound (e.g., upper or lower) can be predicted; this provides useful information that can be obtained with a minimum amount of work. While the method gives bounds for both the ground and excited states, it can be seen from the present results that the bounds for the excited states are generally less accurate than those of the ground state for the same order determinants. It is also apparent that results for those instances, such as the Yukawa potential for small values of  $\lambda$ , which correspond closely to problems for which the logarithmic derivative can be accurately represented by a rational functional form, the bounds are remarkably tight even for low-order determinants.

Finally, we note that the present method can be applied to other potentials with corresponding results, and because the algorithms are well-suited to algebraic programming techniques (e.g., REDUCE), they can be carried out very rapidly on modest size computers.

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