INTERNATIONAL JOURNAL OF QUANTUM CHEMISTRY, VOL. 46, 319–334 (1993)

Accurate Computation of the Energy Spectrum for Potentials with Multiminima

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Abstract

The eigenvalues of the Schrödinger equation with a polynomial potential are calculated accurately by means of the Rayleigh–Ritz variational method and a basis set of functions satisfying Dirichlet boundary conditions. The method is applied to the well potentials having one, two, and three minima. It is shown, in the entire range of coupling constants, that the basis set of trigonometric functions has the capability of yielding the energy spectra of unbounded problems without any loss of convergence providing that the boundary value α remains greater than a critical value α_{cr}. Only the computation of the nearly degenerate states of multiwell oscillators requires dealing with a relatively large truncation order. © 1993 John Wiley & Sons, Inc.

1. Introductory Remarks

The dimensionless Schrödinger equation for a particle of unit mass moving in a polynomial potential $V(x)$

$$\left[-\frac{d^2}{dx^2} + V(x) \right] \Psi(x) = E\Psi(x), \qquad x \in (-\infty, \infty) \tag{1.1}$$

has evoked a great deal of interest owing to its varied applications in quantum field theory and molecular chemistry. Several methods have been proposed for treating such problems. In a very recent paper [1] (hereafter referred to as PI), it was shown by numerical experiments that the eigensolution of the Dirichlet boundary value problem, where the wave function obeys the conditions

$$\Psi(-\alpha) = \Psi(\alpha) = 0 \tag{1.2}$$

can be effectively used to find the spectrum of an unbounded problem. In PI, a critical distance α_{cr} was defined, and it was shown that the low-lying energies $E_n(\alpha)$ are equal to those of $\alpha = \infty$ to 30 digits if the boundedness parameter α is in the near vicinity of α_{cr}. A fairly detailed numerical application was made in PI to the quartic anharmonic oscillator, where $V(x) = x^2 + \beta x^4$, and it was suggested that the method could be extended to arbitrary polynomial potentials.

In this paper, we employ the Rayleigh–Ritz variational method and a basis set of trigonometric functions similar to that of PI, in order to solve both single-well problems and multiwell oscillator problems with degenerate minima. The symmetric

 CCC 0020-7608/93/020319-16

potentials considered here are the single-well oscillator:

$$V(x) = \nu_{2k}x^{2k}, \qquad k = 1 - 5, \qquad \nu_{2k} > 0, \tag{1.3}$$

the two-well oscillator:

$$V(x) = -\nu_2 x^2 + \nu_4 x^4, \qquad \nu_2, \nu_4 > 0, \tag{1.4}$$

and the more complicated anharmonic oscillator:

$$V(x) = \nu_2 x^2 + \nu_4 x^4 + \nu_6 x^6, \qquad \nu_6 > 0, \tag{1.5}$$

which has three minima if appropriate relations between the coupling constants ν_i hold.

The potential (1.3) for $k = 1$ is the well-known harmonic oscillator problem that is exactly solvable for $x \in (-\infty, \infty)$. In spite of this fact it is still of interest, especially for testing various numerical methods [2–6]. The bounded harmonic oscillator was also studied in several works [7–9]. For $k = 2$, both bounded and unbounded versions of the pure quartic oscillator were investigated in [10–14]. To the author's knowledge, however, accurate eigenvalues of the pure sextic, $V(x) = \nu_6 x^6$, the pure octic, $V(x) = \nu_8 x^8$, and the pure dectic, $V(x) = \nu_{10} x^{10}$, oscillators have not been reported previously, although there are good upper and lower bounds from the work of Crandall and Reno [15].

The two-well oscillator $V(x) = -\nu_2 x^2 + \nu_4 x^4$ (Fig. 1) has attracted the attention of scientists for a long time. The very interesting property of its energy spectrum is that the lower eigenvalues are closely bunched in pairs if the two wells are sufficiently separated. This situation occurs for weak coupling when $\nu_4/\nu_2 \ll 1$ and means that the potential has nearly degenerate minima. Thus, the determination of the shift in energy levels due to tunneling through a potential barrier becomes more important. In such a case, the gap between the nearly degenerate eigenvalues has been investigated by the WKB approximation [16], by the path-integral approach [17], and by perturbation theory at large orders [18]. Banerjee and Bhatnagar [19], on the other hand, presented accurate results for the eigenvalues by using an appropriately scaled expansion basis and a recursive series method. Isaacson et al. used an alternative Rayleigh–Ritz method for single- and double-well potentials with symmetrized oscillator functions [20]. More recently, a two-step approach and a JWKB approximation have been proposed by Hsue and Chern [21] and Sanchez and Bejarano [22], respectively, and applied to the two-well oscillator. In this work, we shall consider both the regimes of small and of large ν_4/ν_2 values.

The doubly anharmonic oscillator $V(x) = \nu_2 x^2 + \nu_4 x^4 + \nu_6 x^6$ is another interesting model dealt with in this paper. This potential has been studied by using the theory of continued fractions [23] and asymptotic series for wave functions and energy levels [24]. However, the construction of its exact solutions has received considerably more attention [25–29]. Actually, the wave function of the ground state must vanish as $x \to \pm\infty$ and must not have nodes. We can thus choose as our trial function

$$\Psi_0(x) = \exp\left(-\frac{1}{4}c_4 x^4 + \frac{1}{2}c_2 x^2\right), \qquad c_4 > 0 \tag{1.6}$$

Substituting this into (1.1), we see that (1.6) is an exact eigenfunction with the corresponding eigenvalue expressible as

$$E_0 = -c_2, \tag{1.7}$$

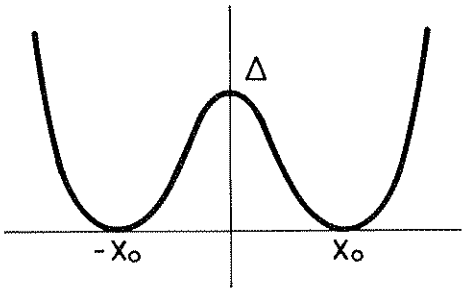

Figure 1. The shifted two-well oscillator: $x_0 = [\nu_2/(4\nu_4)]^{1/2}, \Delta = \nu_2^2/(4\nu_4)$.

subject to a constraint on ν_2,

$$\nu_2 = c_2^2 - 3c_4, \tag{1.8}$$

where

$$c_4 = \nu_6^{1/2}, \qquad c_2 = -\frac{1}{2}\nu_4\nu_6^{-1/2}. \tag{1.9}$$

The other exact states are characterized by exponentially weighted polynomial wave functions. This class of exact solutions is denumerably infinite but not complete.

Furthermore, the potential (1.5) gives a more general type of eigenvalue problem involving three eigenvalue parameters. The potential has no extrema for positive values of coupling constants, except for a single minimum located at the origin. However, for $\nu_4 < 0$ and $\nu_2, \nu_6 > 0$, the potential possesses multiminima and maxima depending on certain algebraic relations between the relative magnitudes of ν_4^2 and $\nu_2\nu_6$ (Fig. 2). It is clear that two negative minima located symmetrically about $x = 0$ appear when $\nu_4^2 > 4\nu_2\nu_6$ [Fig. 2(i)]. The two minima are tangent to the x-axis if $\nu_4^2 = 4\nu_2\nu_6$ [Fig. 2(ii)]. There are two positive minima in the case of $3\nu_2\nu_6 < \nu_4^2 < 4\nu_2\nu_6$ [Fig. 2(iii)]. The potential has inflection points for $\nu_4^2 = 3\nu_2\nu_6$, and again only a single minimum at the origin appears provided that $\nu_4^2 < 3\nu_2\nu_6$. Thus, the potential $V(x) = \nu_2x^2 + \nu_4x^4 + \nu_6x^6$ possesses three minima if and only if $\nu_4 < 0$ and $\nu_4^2 > 3\nu_2\nu_6$. In this paper, the computations will be carried out for these more interesting cases.

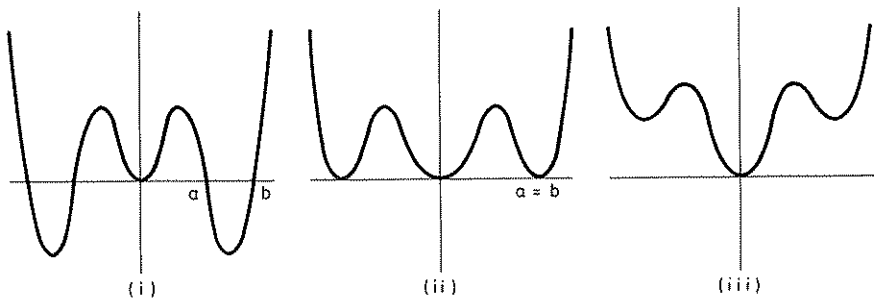

Figure 2. The three-well oscillators.

In the rest of this paper, Section 2 briefly reviews the variational method. Section 3 reports the extremely accurate numerical results for the aforementioned eigenvalue problems. The last section includes a detailed discussion of the present results.

2. The Variational Method

Owing to the fully symmetric structure of the potentials considered in this study, we can use even and odd trial functions separately, to avoid large matrices. If we use the orthonormal basis sets

$$\phi_m(x) = \alpha^{-1/2} \cos\left(m - \frac{1}{2}\right) \frac{\pi}{\alpha} x, \qquad m = 1,2,\ldots \tag{2.1}$$

and

$$\phi_m(x) = \alpha^{-1/2} \sin m\frac{\pi}{\alpha} x, \qquad m = 1,2,\ldots \tag{2.2}$$

for even and odd parity states, respectively, the trial function

$$\Psi_T(x) = \sum_{m=1}^{\infty} f_m \phi_m(x) \tag{2.3}$$

satisfies the Dirichlet boundary conditions $\Psi_T(-\alpha) = \Psi_T(\alpha) = 0$, where the f_m are linear combination coefficients. The substitution of (2.3) into the differential equation

$$\left(-\frac{d^2}{dx^2} + \sum_{i=1}^{M} v_{2i} x^{2i}\right)\Psi(x) = E\Psi(x) \tag{2.4}$$

and the use of the variational principle yield the secular equations

$$\sum_{n=1}^{\infty} (H_{mn} - E\delta_{mn}) f_n = 0, \qquad m = 1,2,\ldots, \tag{2.5}$$

where δ_{mn} is Kronecker's delta and H_{mn} stands for the elements of the variational matrix defined by

$$H_{mn} = -\left\langle \frac{d^2\phi_m}{dx^2}, \phi_n \right\rangle + \sum_{i=1}^{M} v_{2i} \langle x^{2i}\phi_m, \phi_n \rangle . \tag{2.6}$$

If the inner products are evaluated, we then find that

$$H_{mn} = \left(m - \frac{1}{2}\right)^2 \frac{\pi^2}{\alpha^2} \delta_{mn} + \sum_{i=1}^{M} \left(\frac{\alpha}{\pi}\right)^{2i} v_{2i} \left[R^{(i)}_{m+n-1} + R^{(i)}_{m-n}\right] \tag{2.7}$$

for even parity states and

$$H_{mn} = \frac{m^2\pi^2}{\alpha^2} \delta_{mn} + \sum_{i=1}^{M} \left(\frac{\alpha}{\pi}\right)^{2i} v_{2i} \left[R^{(i)}_{m-n} - R^{(i)}_{m+n}\right] \tag{2.8}$$

for odd parity states [1]. Here, $R^{(i)}_k$ is given by

$$R^{(i)}_k = \frac{1}{\pi} \int_0^{\pi} x^{2i} \cos kx \, dx, \tag{2.9}$$

TABLE I. Critical distances α_{cr} and energy eigenvalues E_n of single-well oscillators, $V(x) = x^{2k}$, as a function of k.

k	α_{cr}	n	N	E_n
1	10	0	30	1.000 000 000 000 000 000 000 000 000 000 00
		2	30	5.000 000 000 000 000 000 000 000 000 000 00
		4	30	9.000 000 000 000 000 000 000 000 000 000 00
		6	35	13.000 000 000 000 000 000 000 000 000 000 0
		8	35	17.000 000 000 000 000 000 000 000 000 000 0
2	5.5	0	30	1.060 362 090 484 182 899 647 046 016 69
		2	35	7.455 697 937 986 738 392 156 591 347 19
		4	35	16.261 826 018 850 225 937 894 954 430 4
		6	35	26.528 471 183 682 518 191 813 828 183 7
		8	40	37.923 001 027 033 985 146 516 378 551 9
3	3.75	0	35	1.144 802 453 797 052 763 765 457 534 15
		2	40	9.073 084 560 921 433 856 016 249 096 66
		4	40	21.714 165 422 196 722 281 689 785 148 6
		6	40	37.613 086 560 895 160 889 601 543 047 5
		8	40	56.199 300 852 499 359 421 090 060 527 1
4	3.15	0	45	1.225 820 113 800 492 191 591 086 026 63
		2	45	10.244 946 977 236 854 744 232 174 213 0
		4	45	25.809 006 751 297 331 886 444 795 462 1
		6	50	46.312 770 495 037 273 953 671 286 595 1
		8	50	71.039 257 675 878 442 936 631 970 079 7
5	2.75	0	50	1.298 843 700 678 521 375 512 300 164 66
		2	55	11.154 318 202 156 246 849 971 760 449 8
		4	55	28.971 467 212 683 700 397 910 508 847 2
		6	55	53.192 305 771 130 587 955 968 056 186 2
		8	55	83.014 287 075 568 004 814 542 010 610 5

which results in

$$R_k^{(i)} = \sum_{p=0}^{i-1} \frac{(-1)^{p+k}}{k^{2(p+1)}} \binom{2i}{2p+1} (2p+1)!\, \pi^{2(i-1-p)}, \qquad k > 0 \tag{2.10a}$$

$$R_0^{(i)} = \frac{\pi^{2i}}{2i+1}, \qquad k = 0. \tag{2.10b}$$

Furthermore, it is possible to derive a recurrence relation of form

$$k^2 R_k^{(i)} = 2i\pi^{2(i-1)}(-1)^k - 2i(2i-1)R_k^{(i-1)}, \qquad i \geq 1, \tag{2.11}$$

with the initial condition $R_k^{(0)} = 0$; this is computationally more useful than the explicit formula (2.10a).

3. Numerical Results

Numerical computations employed quadruple precision arithmetic on a VAX-11/780 computer. Present results for the eigenvalues of the well potentials are exact up to the last figure. The symmetric variational matrices (2.7) and (2.8) are diagonalized by the standard routines TRED2 and TQL2 [30]. The results correspond to the even and odd parity state energies, respectively.

In numerical tables, n shows the quantum number of the state and N stands for the number of basis functions required to obtain the desired accuracy. The critical distances α_{cr} or l_{cr}, at which the asymptotic energies can be calculated to 30 digits, are also included in the tables. Such distances may be found in a finite-difference procedure when the calculation is allowed to "find its own infinity" [31].

Within this framework, Table I contains the energy eigenvalues of the single-well oscillator $V(x) = v_{2k}x^{2k}$ as a function of k. We present only the even parity states since the spectrum of such potentials is numerically well isolated, with none of the eigenvalues close to each other. It is clear that the coefficients v_{2k} can be set to unity. This specification does not create any loss of generality, since a linear scaling transformation on x transforms any case to $v_{2k} = 1$.

For the double-well case, the potential $V(x) = -v_2x^2 + v_4x^4$ may be investigated in the form $V(x) = -x^2 + \beta x^4$. With the transformation of variable from x to $v_2^{1/4}x$, we deduce that the Hamiltonian $H(v_2, v_4)$ has the scaling properties

$$H(v_2, v_4) = v_2^{1/2}H(1, \beta) \tag{3.1a}$$

$$E(v_2, v_4) = v_2^{1/2}E(1, \beta) \tag{3.1b}$$

$$\alpha_{cr}(v_2, v_4) = v_2^{-1/4}\alpha_{cr}(1, \beta), \tag{3.1c}$$

where the effective single parameter of the problem is defined by

$$\beta = v_2^{-3/2}v_4. \tag{3.2}$$

Thus, it is more convenient to consider the reduced potential $V(x) = -x^2 + \beta x^4$. Moreover, the operator shifted by $1/(4\beta)$ is now positive definite. Therefore, the results are given in terms of $E(1, \beta) + 1/(4\beta)$. In Table II, we present the nearly degenerate eigenvalues for the case of $\beta = 0.01$. The ground and the first five excited states of the symmetric two-well oscillator for larger couplings are reported in Table III as β varies from 0.05 to 100.

Numerical Tables IV–VIII are devoted to the doubly anharmonic oscillator with three minima. We deal only with the case of $v_4^2 \geq 4v_2v_6$ [Fig. 2(i, ii)], where the potential is of the form

$$V(x) = v_2x^2 - v_4x^4 + v_6x^6, \qquad v_2, v_4, v_6 > 0. \tag{3.3}$$

As can be readily seen, such a polynomial has four real roots located at the points $x = \mp a$ and $x = \mp b$ satisfying the relations $a^2 + b^2 = v_4/v_6$ and $a^2b^2 = v_2/v_6$. If $v_4^2 = 4v_2v_6$, then $a = b$. Therefore, the potential (3.3) may be rewritten in the form

$$V(x) = v_6x^2(x^2 - a^2)(x^2 - b^2) = b^6v_6\left(\frac{x}{b}\right)^2\left[\left(\frac{x}{b}\right)^2 - \frac{a^2}{b^2}\right]\left[\left(\frac{x}{b}\right)^2 - 1\right], \tag{3.4}$$

which implies introduction of a new variable ξ:

$$\xi = \frac{x}{b}, \qquad \xi \in \left[-\frac{\alpha}{b}, \frac{\alpha}{b}\right]. \tag{3.5}$$

TABLE II. Nearly degenerate states of the two-well oscillator for $\beta = 0.01$, where $\alpha_{cr} = 15$.

n	N	$E_n + 25 = E_n + 1/(4\beta)$
0	55	1.404 048 605 297 706 882 425 707 570 82
1	55	1.404 048 605 297 706 888 602 566 280 56
2	55	4.170 193 605 999 310 127 833 875 071 30
3	55	4.170 193 605 999 310 219 613 291 198 73
4	55	6.870 088 833 714 024 612 172 315 168 49
5	55	6.870 088 833 714 046 802 425 995 681 89
6	55	9.498 578 387 187 870 055 194 418 356 55
7	55	9.498 578 387 191 178 212 320 856 961 14
8	55	12.049 309 486 334 092 592 332 880 171 6
9	55	12.049 309 486 673 006 847 573 312 477 9
10	60	14.514 205 022 981 239 103 429 421 443 9
11	60	14.514 205 048 121 017 338 991 612 415 8
12	60	16.882 545 691 994 146 580 799 215 687 4
14	60	19.139 166 710 066 626 391 288 691 125 7
15	60	19.139 223 296 295 250 364 092 982 015 3
16	60	21.259 651 806 114 797 518 951 274 698 5
17	60	21.261 337 849 110 831 987 157 265 245 7
18	65	23.184 249 060 436 658 552 728 486 119 9
19	65	23.218 098 293 156 870 760 576 623 817 4
20	65	24.705 339 712 918 880 372 982 237 097 0
21	65	25.024 274 304 596 992 258 984 339 940 8

The problem is therefore altered to

$$\left[-\frac{d^2}{d\xi^2} + \beta_1^2\xi^2(\xi^2 - \beta_2^2)(\xi^2 - 1)\right]\Psi(\xi) = b^2E\Psi(\xi), \tag{3.6}$$

which involves two eigenvalue parameters such that

$$\beta_1 = b^4\nu_6^{1/2}, \qquad \beta_1 > 0 \tag{3.7}$$

and

$$\beta_2 = \frac{a}{b}, \qquad 0 < \beta_2 \leq 1. \tag{3.8}$$

According to our previous formalism, Eq. (3.6) is expressible as

$$\left[-\frac{d^2}{d\xi^2} + a_2\xi^2 - a_4\xi^4 + a_6\xi^6\right]\Psi(\xi) = \lambda\Psi(\xi), \qquad \xi \in [-l, l], \tag{3.9}$$

where we set

$$l = \frac{\alpha}{b}, \qquad \lambda = b^2E \tag{3.10}$$

and

$$a_2 = \beta_1^2\beta_2^2, \qquad a_4 = \beta_1^2(1 + \beta_2^2), \qquad a_6 = \beta_1^2. \tag{3.11}$$

We can get back to the original coupling constants ν_2, ν_4, and ν_6 with the assistance of the scaling relationships

$$\nu_2 = b^{-4}a_2, \qquad \nu_4 = b^{-6}a_4, \qquad \nu_6 = b^{-8}a_6. \tag{3.12}$$

TABLE III. Critical distances and energy eigenvalues of two-well oscillators, $V(x) = -x^2 + \beta x^4$, as a function of β.

β	α_{cr}	n	N	$E_n + 1/(4\beta)$
0.05	10	0	40	1.358 422 103 747 795 462 828 858 001 13
		1	40	1.360 133 597 773 303 267 604 942 031 88
		2	40	3.746 917 080 727 930 707 382 042 658 90
		3	40	3.848 838 300 057 397 949 123 848 305 50
		4	40	5.369 059 360 284 711 606 322 475 533 06
		5	40	6.177 383 138 505 279 684 894 921 225 05
0.1705	7.5	0	35	1.005 907 534 732 669 494 259 934 270 98
		1	35	1.465 359 922 207 691 593 693 811 222 26
		2	35	3.120 683 690 166 030 901 005 016 518 38
		3	35	4.822 552 955 752 771 227 915 786 027 28
		4	35	6.876 623 854 334 680 478 308 869 928 84
		5	35	9.160 917 456 892 154 940 661 345 803 18
1	5	0	30	0.907 653 005 180 715 123 059 021 723 111
		1	30	3.084 536 202 119 304 214 654 676 208 75
		2	30	6.413 901 256 963 068 240 915 237 315 02
		3	30	10.288 646 120 711 576 043 356 901 150 3
		4	30	14.622 406 504 677 868 955 906 567 619 7
		5	30	19.335 714 685 024 187 731 696 964 367 6
10	3.5	0	30	2.137 877 898 050 259 289 303 800 668 73
		1	30	7.786 789 928 304 487 098 125 425 821 37
		2	30	15.505 390 136 564 835 078 358 830 039 9
		3	30	24.384 990 424 717 251 665 235 908 096 4
		4	35	34.200 530 589 304 058 305 960 711 826 1
		5	35	44.799 925 053 756 998 370 766 133 927 4
100	2.35	0	30	4.845 921 891 362 033 319 865 475 050 73
		1	30	17.444 197 413 120 973 381 603 569 929 0
		2	30	34.340 152 315 559 552 006 178 212 246 2
		3	30	53.716 507 749 978 459 831 972 443 757 7
		4	35	75.085 977 797 358 526 304 872 975 386 8
		5	35	98.128 314 922 737 976 133 113 220 257 5

By this representation of the potential in terms of β_1 and β_2, it is now more suitable to investigate systematically a very wide class of three-well oscillators.

The parameters of the potentials that have been treated in this work is given in Table IV. It is seen that β_1 changes from 0.1 to 100. For each β_1, almost the entire range of β_2, $0 < \beta_2 \leq 1$, is covered by taking $\beta_2 = 0.25$, 0.5, 0.75, and 1. Table IV also includes the scaled coupling constants a_2, a_4, and a_6 and the critical distances l_{cr} determined by numerical experiments. Tables V–VIII present the energy eigenvalues for β_1 values of 0.1, 1, 10, and 100, respectively, as a function of β_2. Further results are available from the author.

4. Discussion

In this article, we have calculated the energy eigenvalues to 30 digits for single-, double-, and triple-well oscillators. We have utilized a Rayleigh–Ritz variational method with a trigonometric trial function satisfying Dirichlet boundary conditions in order to characterize the wave function. The spectra of unbounded oscillators are obtained by way of determining the critical boundary value α_{cr} at which the

TABLE IV. Critical distances and parameters for symmetric three-well potentials, $V(x) = a_2\xi^2 - a_4\xi^4 + a_6\xi^6$, that have been considered in this work.

β_1	β_2	a_2	a_4	a_6	l_{cr}
0.1	0.25	0.000625	0.010625	0.017	
	0.5	0.0025	0.0125	0.017	
	0.75	0.005625	0.015625	0.017	
	1	0.01	0.02	0.017	
1	0.25	0.0625	1.0625	1	4
	0.5	0.25	1.25	1	4
	0.75	0.5625	1.5625	1	4
	1	1	2	1	4
10	0.25	6.25	106.25	100	2.25
	0.5	25	125	100	2.25
	0.75	56.25	156.25	100	2.25
	1	100	200	100	2.25
100	0.25	625	10,625	10,000	1.5
	0.5	2,500	12,500	10,000	1.5
	0.75	5,625	15,625	10,000	1.5
	1	10,000	20,000	10,000	1.5

boundedness effect can be neglected within a precision of $\epsilon = 10^{-30}$. This means in

TABLE V. Energy eigenvalues of three-well oscillators for which $\beta_1 = 0.1$, as a function of β_2.

β_2	n	N	λ_n
0.25	0	40	0.335 307 026 446 298 957 015 526 159 333
	1	40	1.287 110 666 358 014 585 506 963 448 47
	2	45	2.724 811 069 636 117 883 128 640 525 60
	3	45	4.522 212 252 801 926 241 946 683 868 23
	4	45	6.609 220 487 761 567 182 040 296 892 00
	5	45	8.951 237 917 331 980 654 084 605 733 30
0.5	0	40	0.332 116 066 854 572 291 094 228 348 607
	1	40	1.275 553 314 002 056 240 034 119 051 34
	2	40	2.703 526 109 589 289 247 940 196 718 40
	3	40	4.491 717 977 552 185 005 048 570 920 19
	4	40	6.569 363 549 227 674 344 004 128 773 63
	5	40	8.901 944 681 037 717 945 153 326 746 26
0.75	0	40	0.326 645 214 722 982 248 002 468 553 370
	1	40	1.255 853 805 046 198 422 073 930 643 76
	2	40	2.667 436 012 514 089 230 854 613 924 84
	3	40	4.440 184 663 233 381 652 222 278 882 27
	4	40	6.502 181 794 358 978 131 859 394 550 86
	5	40	8.818 898 973 884 978 753 087 199 875 64
1	0	40	0.318 643 268 791 198 865 205 457 459 093
	1	40	1.227 304 410 786 912 506 557 783 174 75
	2	40	2.615 564 864 492 694 881 454 901 628 20
	3	40	4.366 501 625 615 184 730 872 620 528 28
	4	40	6.406 274 504 379 244 660 515 793 874 41
	5	40	8.700 720 053 739 730 114 276 862 784 54

TABLE VI. Energy eigenvalues of three-well oscillators for which $\beta_1 = 1$, as a function of β_2.

β_2	n	N	λ_n
0.25	0	40	0.854 669 975 506 280 847 213 537 311 741
	1	40	3.429 073 560 937 156 859 841 939 081 58
	2	40	7.552 427 309 905 065 158 118 406 839 10
	3	40	12.845 094 060 891 739 719 823 985 571 3
	4	45	19.048 644 993 382 372 287 852 900 291 8
	5	45	26.058 863 040 156 756 193 494 175 019 9
0.5	0	40	0.858 170 060 798 353 154 176 393 017 907
	1	40	3.387 423 710 020 843 304 586 270 615 66
	2	40	7.424 465 391 338 748 423 945 723 384 54
	3	40	12.639 593 826 406 929 780 939 321 952 5
	4	40	18.761 936 372 200 498 211 435 141 452 3
	5	40	25.688 709 919 154 881 415 295 413 974 1
0.75	0	40	0.861 062 938 121 661 908 094 126 564 928
	1	40	3.307 111 458 904 039 770 721 335 794 05
	2	40	7.193 850 655 694 506 452 887 888 752 36
	3	40	12.276 899 552 793 310 442 498 464 225 1
	4	40	18.261 032 877 984 289 837 728 035 327 7
	5	40	25.045 974 703 319 195 661 405 477 402 2
1	0	40	0.857 327 047 099 475 918 361 970 229 431
	1	40	3.166 872 848 343 639 676 676 609 183 13
	2	45	6.828 838 167 600 950 705 941 586 442 10
	3	45	11.722 080 498 421 764 096 018 747 383 1
	4	45	17.506 892 284 989 833 841 949 814 101 0
	5	45	24.087 465 342 163 223 260 970 975 943 8

the computational sense that such an α_{cr} value represents infinity. It is noteworthy that the method rapidly converges and its rate of convergence appears numerically to remain unchanged, for α values in the vicinity of α_{cr}. Indeed, all computations made here confirm this argument, which was first suggested and tested in PI. A more precise estimate of the critical distances than the tabulated ones is thus unnecessary. On the other hand, the critical boundary value of the two-well and the three-well oscillators can be roughly approximated by using the simple scaling relation, $\alpha_{cr} \nu_{2k}^{-1/(2k+2)}$, where ν_{2k} is the dominant coupling constant and α_{cr} is the critical distance of the potential $V(x) = x^{2k}$ given in Table I. Thus, the estimation of the α_{cr} value of a specific polynomial having the asymptotic behavior x^{2k} is not a problematic aspect of the method.

In a recent paper by Meson et al. [32], a similar basis set of trigonometric functions has been proposed to calculate the eigenvalues of the generalized anharmonic oscillators, $V(x) = \omega^2 x^2 + \beta x^{2m}$, $m = 2, 3, \ldots$. Since the Hamiltonian of the problem describes a particle moving inside a box of length two units bounded with impenetrable walls located at $x = \pm 1$ when $m \to \infty$, $\beta = 1$, and ω vanishes, they claimed that the trigonometric basis set could be appropriate if m is large enough; they gave numerical results for $m = 3$ and $m = 4$. On the contrary, our numerical results given for the $V(x) = x^{2k}$ oscillator do not show this trend (Table I). As k increases, the critical distance of α decreases due to the contraction of the potential, which implies that α_{cr} tends to its limiting value $\alpha_{cr} = 1$. However, it is observed from Table I that the

algorithm provides the best converged results in the case of the harmonic oscillator $V(x) = x^2$. Furthermore, the rate of convergence falls off rapidly when k increases. More specifically, the number of basis function required to reach 30 digits accuracy for the harmonic oscillator is $N = 30$, whereas the same accuracy requires 50–55 basis functions for the dectic oscillator $V(x) = x^{10}$. Hence, we may suggest, contrary to Meson et al. [32], that the trigonometric basis set is satisfactorily used for treating all polynomial potentials with an asymptotic behavior proportional to x^{2k} if k is not very large. Otherwise, the larger the k, the larger the dimension of the variational matrix required. The diagonalization of a matrix beyond a certain size is, however, intractable.

The ground-state eigenvalues in Table I are in excellent agreement with the upper- and lower-bound results of Crandall and Reno [15]. Such an investigation of the potential $V(x) = x^{2k}$ is of stimulative interest. We can now expect that the convergence rate in the case of the two-well oscillator $V(x) = -x^2 + \beta x^4$ should be similar to that for the potential $V(x) = x^4$. We see from Table I that 30–35 basis functions are sufficient to obtain the desired precision for $V(x) = x^4$. Similarly, the eigenvalues of the two-well oscillator for $\beta \geq 0.1705$ stabilize when $N = 30$–35 (Table III). The variation of β affects only the critical distances of α. As an exceptional case, a slowing down of convergence is obviously seen for small couplings whenever there are four classical turning points in certain cases of the quantum number n. In the regime of $\beta \leq 0.1705$, the lower eigenvalues are close to each other in pairs owing to the tunneling through the potential barrier. The number of such pairs are ten, two, and one for $\beta = 0.01$, 0.05, and 0.1705, respectively (Tables II and III). When $\beta = 0.1705$, the maximum value of the shifted potential is $\Delta = 1.466$ and there exist four classical turning points $V(x) = E$ only for the ground and the first exited states. $\beta = 0.1705$ is thus a threshold value after which the number of turning points reduces to two and the probability of tunneling approaches zero.

In spite of dealing with a relatively large truncation order in the small β-regime, the present method is as precise as in the other cases. If we recall the fact that many methods fail for potentials with degenerate minima [11, 17], the power of the trigonometric basis set in obtaining the nearly degenerate eigenvalues with such an accuracy is quite impressive. Comparison shows that the eigenvalues calculated by Banerjee and Bhatnagar [19] agree with our results to the accuracy quoted.

The numerical results tabulated in detail show that the method can be extended with an arbitrarily high accuracy to the triple-well case (Tables V–VIII). In the wide range of the eigenvalue parameters β_1 and β_2, we see that the acceleration of the convergence is similar to that for the pure sextic oscillator $V(x) = x^6$. Again, this confirms that one of the most effective features on the convergence of the method is the asymptotic behavior of the potential under consideration. However, in order to give further comments on the three-well oscillators, we need some additional information about the potential function. A knowledge of extremum values is sufficient to this end. Maximum and minimum values of $V(\xi) = \beta_1^2 \xi^2 (\xi^2 - \beta_2^2)(\xi^2 - 1)$ can be reached at the points $\xi = \pm\xi_0, \pm\xi_1$, where

$$\xi_0^2 = \frac{1}{3}\left[1 + \beta_2^2 - (1 - \beta_2^2 + \beta_2^4)^{1/2}\right],$$

TABLE VII. Energy eigenvalues of three-well oscillators for which $\beta_1 = 10$, as a function of β_2.

β_2	n	N	λ_n
0.25	0	45	−2.144 142 136 157 253 649 145 754 388 76
	1	45	−0.046 021 821 201 495 577 767 704 090 147 7
	2	45	10.111 965 267 772 315 974 265 604 062 0
	3	45	22.941 173 527 531 557 527 700 375 158 6
	4	45	38.213 051 604 415 762 444 281 085 078 1
	5	45	56.174 747 620 357 614 094 101 640 564 2
0.5	0	45	0.423 545 280 494 471 297 861 935 010 377
	1	45	3.223 559 130 917 617 976 049 702 265 34
	2	45	11.672 319 849 048 966 947 213 389 530 9
	3	45	24.554 796 097 684 641 027 666 177 011 7
	4	45	39.475 830 006 202 543 553 667 911 199 3
	5	45	56.931 170 613 938 735 906 519 020 550 6
0.75	0	45	3.996 711 883 686 471 105 192 935 317 95
	1	45	8.359 323 762 938 682 330 647 171 444 69
	2	45	14.438 160 906 153 948 176 552 018 127 7
	3	45	26.831 957 379 451 268 296 903 467 057 0
	4	45	41.157 191 184 328 575 093 423 974 083 3
	5	45	57.658 083 192 268 668 745 879 771 582 6
1	0	45	7.608 748 395 957 152 937 532 052 985 28
	1	45	14.312 152 647 125 366 051 432 781 614 2
	2	45	17.701 077 230 158 836 759 357 141 618 7
	3	45	28.735 992 048 284 744 389 180 155 113 2
	4	45	42.325 641 967 403 269 446 383 458 269 7
	5	45	57.186 591 978 338 673 787 917 956 380 0

$$\xi_1^2 = \frac{1}{3}\left[1 + \beta_2^2 + (1 - \beta_2^2 + \beta_2^4)^{1/2}\right], \tag{4.1}$$

and are equal to $V_{\max} = V(-\xi_0) = V(\xi_0)$ and $V_{\min} = V(-\xi_1) = V(\xi_1)$, respectively. Numerical values of $V_{\max}$ and $V_{\min}$ are given in Tables IX as a function of β_1 and β_2. We now deduce from Tables V, VI, and IX that the number of classical turning points, the high potential beyond which prevents tunneling, are two in the case of $\beta_1 < 10$, being independent of β_2. In this regime of β_1, the eigenvalues stabilize when $N = 40$–45. For $\beta_1 \geq 10$, the number of turning points $V(\xi) = \lambda$ becomes four or six in certain cases of n. For $\beta_1 = 100$, the spectrum of the three-well oscillator possesses an interesting nature. For this reason, we have included more quantum states in Table VIII. We observe from this table that the lower eigenvalues are ordered in pairs for $\beta_2 \leq 0.5$, as in the double-well case. For $\beta_2 > 0.5$, the remarkable effect of the central well is clearly shown. It is also clear that the computation of the nearly degenerate eigenvalues requires a larger value of N.

The eigenvalues obtained by means of the Dirichlet boundary value problem are upper bounds to the exact unbounded eigenvalues, so that a systematic investigation on the boundary value α provides a very good check on the accuracy of the results. Furthermore, it is known that the eigenvalues of the von Neumann boundary value problem

$$H\Psi(x) = E\Psi(x), \qquad \Psi'(-\alpha) = \Psi'(\alpha) = 0 \tag{4.2}$$

TABLE VIII. Energy eigenvalues of three-well oscillators for which $\beta_1 = 100$, as a function of β_2.

β_2	n	N	λ_n
0.25	0	60	−1184.875 326 186 040 740 344 585 135 76
	1	60	−1184.875 326 186 040 740 312 064 459 48
	2	65	−883.276 315 720 872 020 227 881 486 583
	3	65	−883.276 315 720 871 741 965 530 344 567
	4	65	−607.163 496 718 315 409 276 377 708 634
	5	65	−607.163 496 717 189 289 637 628 428 736
	6	70	−360.887 954 337 848 639 620 600 876 825
	7	70	−360.887 951 469 771 638 089 679 874 408
	8	70	−152.159 114 323 489 920 947 814 923 708
	9	70	−152.153 940 833 194 009 879 331 806 850
0.5	0	65	−790.585 705 216 079 643 338 596 233 435
	1	65	−790.585 705 216 079 642 531 515 180 949
	3	65	−495.071 566 736 786 847 564 696 115 182
	4	65	−230.179 480 410 971 124 132 451 586 775
	5	65	−230.179 480 099 118 075 058 065 245 389
	6	70	−5.044 017 759 142 943 067 336 535 855 19
	7	70	−5.031 334 305 097 900 834 048 485 199 54
0.75	0	65	−217.466 334 381 900 222 273 752 983 930
	1	65	−217.466 334 381 900 170 359 029 336 219
	2	55	72.814 067 298 465 218 079 373 806 469 9
	3	65	88.395 512 010 972 270 193 680 088 672 2
	4	65	88.395 512 398 082 883 823 841 713 938 0
	5	55	213.657 578 332 372 658 733 130 130 401
	6	60	343.956 820 391 174 797 916 660 839 617
	7	70	357.244 165 194 238 403 670 888 908 641
	8	70	357.269 937 779 705 822 146 816 196 682
1	0	45	98.464 158 830 285 882 641 440 488 793 6
	1	70	196.128 280 065 559 346 604 425 403 078
	2	70	196.128 280 065 559 346 763 113 401 238
	3	50	292.189 612 804 079 776 291 190 713 117
	4	50	479.266 089 938 645 404 331 241 880 603
	5	70	570.144 566 033 208 140 811 664 580 736
	6	70	570.144 566 033 313 025 752 666 013 011

are lower bounds to the exact unbounded eigenvalues if α is greater than the root of the equation $V(\alpha) - E_n = 0$ [32, 34]. This means that α must lie beyond the classical turning points. Hence, the accuracy of the results may also be tested by employing the lower bounds. For this purpose, we have solved the von Neumann boundary value problem (4.2), which may be worked out in a similar fashion. In this case, we use the orthonormal basis sets

$$\phi_m(x) = \alpha^{-1/2}[1 + \delta_{m1}(2^{-1/2} - 1)]\cos(m - 1)\frac{\pi}{\alpha}x, \qquad m = 1, 2, \ldots \tag{4.3}$$

for even parity states and

$$\phi_m(x) = \alpha^{-1/2}\sin\left(m - \frac{1}{2}\right)\frac{\pi}{\alpha}x, \qquad m = 1, 2, \ldots \tag{4.4}$$

for odd parity states. In Table X, we report a specimen calculation made for the three-well oscillator with $\beta_1 = 100$ and $\beta_2 = 0.25$; this shows that there is no uncertainty in the accuracy of the tabulated eigenvalues.

TABLE IX. Maximum and minimum values of the potential function $V(\xi) = a_2\xi^2 - a_4\xi^4 + a_6\xi^6$.

β_1	β_2	V_{max}	V_{min}
0.1	0.25	0.000 009	−0.001 343
	0.5	0.000 187	−0.000 947
	0.75	0.000 588	−0.000 380
	1	0.001 481	0
1	0.25	0.000 946	−0.134 373
	0.5	0.013 740	−0.094 759
	0.75	0.058 887	−0.038 090
	1	0.148 148	0
10	0.25	0.094 629	−13.437 366
	0.5	1.374 093	−9.475 945
	0.75	5.888 747	−3.809 030
	1	14.814 814	0
100	0.25	9.462 909	−1343.786 635
	0.5	137.409 335	−947.594 520
	0.75	588.874 726	−380.903 083
	1	1481.481 481	0

TABLE X. A specimen accuracy test for the nearly degenerate states of the three-well oscillator, $\beta_1 = 100$ and $\beta_2 = 0.25$, using the upper and lower bounds to the exact unbounded eigenvalues.

n	l	Condition	N	λ_n
0	1	Dirichlet	20	−1184.155
		v. Neumann	20	−1185.792
	1.25	Dirichlet	45	−1184.875 326 186 040 740 276
		v. Neumann	45	−1184.875 326 186 040 740 414
	1.5	Dirichlet	60	−1184.875 326 186 040 740 344 585 135 76
		v. Neumann	60	−1184.875 326 186 040 740 344 585 135 76
2	1	Dirichlet	30	−879.290
		v. Neumann	30	−888.906
	1.25	Dirichlet	45	−883.276 315 720 872 018 344
		v. Neumann	45	−883.276 315 720 872 021 551
	1.5	Dirichlet	65	−883.276 315 720 872 020 227 881 486 583
		v. Neumann	65	−883.276 315 720 872 020 227 881 486 583
7	1	Dirichlet	35	−341.841
		v. Neumann	35	−389.406
	1.25	Dirichlet	45	−360.887 951 469 771 579
		v. Neumann	45	−360.887 951 469 771 699
	1.5	Dirichlet	70	−360.887 951 469 771 638 089 679 874 408
		v. Neumann	70	−360.887 951 469 771 638 089 679 874 408
9	1	Dirichlet	35	−128.045
		v. Neumann	35	−183.901
	1.25	Dirichlet	45	−152.153 940 833 193 817
		v. Neumann	45	−152.153 940 833 194 209
	1.5	Dirichlet	70	−152.153 940 833 194 009 879 331 806 850
		v. Neumann	70	−152.153 940 833 194 009 879 331 806 850

Consequently, we may suggest that the present method is applicable quite generally for eigenvalue problems having one or more minima and involving one or more eigenvalue parameters. The method may be extended to periodic N-well potentials in the future [35]. The algorithm is quite rapid, and there is no accuracy loss in any regime of the eigenvalue parameters. To give a rough idea about the time consumption, we may say that a run for $N = 40$ consumes approximately one CPU minute. A remarkable slowing down of convergence occurs only due to the existence of nearly degenerate eigenstates. However, it is possible to obtain an arbitrarily high precision depending on the machine accuracy in any case.

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Received April 27, 1992
Revised manuscript received September 14, 1992
Accepted for publication October 12, 1992