

The Influence of the Boundedness of Polynomial Potentials on the Spectrum of the Schrödinger Equation

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1. INTRODUCTION

The analytical as well as numerical studies of the one-dimensional Schrödinger equation for polynomial potentials,

$$H\psi(x) = E\psi(x), \quad \lim_{x \rightarrow \mp\infty} \psi(x) = 0, \quad x \in (-\infty, \infty), \quad (1.1)$$

have been of considerable interest for many years. Here, H stands for the Hamiltonian of the system

$$H = -\frac{d^2}{dx^2} + V(x), \quad V(x) = \sum_{i=1}^{2M} v_i x^i, \quad (1.2)$$

$$M \geq 1, \quad v_{2M} > 0,$$

where $\psi(x)$, E , and the v_i are the wavefunction, energy eigenvalue, and potential coefficients, respectively. Especially, the problem of generalized anharmonic oscillators $V(x) = x^2 + \beta x^{2m}$, $m = 2, 3, \dots$, is the most studied system of this kind.

Perturbative, variational, numerical, recursive, or iterative techniques, as well as Hill determinant and asymptotic WKB methods, are widely employed in the works on anharmonic oscillators [1-9]. It may be proven that the ground state energy perturbation series has a zero radius of convergence due to an essential singularity at the origin in the complex anharmonicity constant, β , plane [7]. So the perturbational studies emphasize the resummation of the divergent Rayleigh-Schrödinger series by using Pade and Pade-Borel summability methods [5, 7].

The general tendency in the other methods is to try to obtain the best approximate wavefunction. For this purpose, it is useful to consider the asymptotic behaviour of the wavefunction $\psi(x)$ for large values of x , the determination of which can be accomplished by writing $\psi(x) = \exp(-cx^p)$. If this expression is substituted into (1.1), the result is

$$-p^2 c^2 x^{2p-2} + p(p-1) c x^{p-2} + \sum_{i=1}^{2M} v_i x^i = E. \quad (1.3)$$

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In order that the leading terms cancel each other out, it is necessary that $p = M + 1$ and $(M + 1)^2 c^2 = v_{2M}$. Since the wavefunction must vanish for $x \rightarrow \mp\infty$, we deduce that the required asymptotic form is $\psi(x) \sim \exp(-(\sqrt{v_{2M}/(M+1)} x^{M+1}))$. In a general situation it is no more difficult to determine the asymptotic behaviour of a wavefunction. But the difficult point is to construct a complete orthonormal set having the specified behaviour [10]. In the case, where M is an even number, there is an additional complication because of the appearance of the "unnatural" function $|x|^{M+1}$ in the exponent. Only in the harmonic oscillator case, for which $M = 1$ and $V(x) = x^2$, there is a complete orthonormal set available in the literature as the exact solution of the problem.

With this general outline of constructing the basis functions, in the aforementioned methods, especially in the variational schemes, the wavefunction is postulated to be of the form [2, 4]

$$\psi(x) = \exp(-\frac{1}{2}x^2) \sum_{n=0}^{\infty} a_n x^n. \quad (1.4)$$

The presence of integration in variational calculations makes it almost impossible to use a well defined trial function that characterizes the true asymptotic form of the wavefunction. It is noteworthy to indicate that in Ref. [1] an integration-free method, namely the Wronskian approach, has been devised. Integration-free character of this method allows one to construct a complicated trial function which satisfactorily reflects the particular behaviour of the exact wavefunction in question. Actually, extremely accurate numerical results have been obtained for the energy eigenvalues of quartic, $x^2 + \beta x^4$, and sextic, $x^2 + \beta x^6$, oscillators in the entire range of β by introducing a novel trial function.

In this work, we are interested solely in the discrete spectrum, and we propose an alternative approach for the determination of the spectral points of the Schrödinger equation.

We assume that the boundaries are at finite points and modify the problem as follows:

$$H\psi(x) = E\psi(x), \psi(-\alpha) = \psi(\alpha) = 0, \quad x \in [-\alpha, \alpha]. \quad (1.5)$$

Thus, we deal with the eigenvalue problem of a polynomial oscillator bounded by infinitely high potentials located at the points $\mp\alpha$. This type of model, on the other hand, has been applied in several fields [11–21]. The standard works on the bounded oscillators are due to Vawter, who used both a WKB and a series method [11, 12]. Among the others, the hypervirial perturbative method is widely used for the investigation of enclosed quantum mechanical systems [14–18].

The principle purpose of the present article is to compute the variances accurately between the spectrum of the usual problem (1.1) and the spectrum of the system (1.5) when the wavefunction obeys Dirichlet boundary conditions. The boundary value α in (1.5) is said to be a parameter which characterizes the boundedness effect on the spectrum of the eigenvalue problem. Hence the numerical experiments are performed for various values of α . It may be noted that the significant advantage of this model is the possibility of the construction of an orthonormal basis set which is not restricted to a particular potential, but also valid for a wide class of both symmetrical and asymmetrical polynomial oscillators. Such a basis set is derived from the exact solution of the eigenvalue problem

$$-F''(x) = \lambda F(x), \quad x \in [a, b], \quad F(a) = F(b) = 0 \quad (1.6)$$

and used in a standard variational scheme. It is not a surprise that the eigenfunction solution in terms of the trigonometric functions of this well known elementary problem has previously been proposed for treating similar kind of problems [20, 21]. But the present strategy, which tries to systematically investigate the boundedness effect and shows numerically the power of the trigonometric basis sets for obtaining the spectrum of unbounded problems with any desired accuracy, seems to be a new approach.

This paper is organized as follows: The evaluation of the matrix elements of the resulting matrix eigenvalue problem is given in Section 2 for a general polynomial potential. The method is then applied to two particular systems. The significant aspects of the present results are pointed out in the last section, which also includes certain remarks and discussions.

2. CONSTRUCTION OF THE VARIATIONAL MATRIX

Instead of taking the symmetric interval in (1.5), it is first useful to deal with the more general case where $x \in [a, b]$. Now with the transformation of variable from x to ξ ,

$$\xi = (x - a)/h, \quad h = (b - a)/\pi, \quad \xi \in [0, \pi], \quad (2.1)$$

the Schrödinger equation becomes

$$\left[-\frac{d^2}{d\xi^2} + h^2 V(\xi) \right] \psi(\xi) = h^2 E \psi(\xi), \quad \psi(0) = \psi(\pi) = 0, \quad (2.2)$$

wherein the potential is altered to

$$V(\xi) = \sum_{i=1}^{2M} \sum_{j=0}^i V_{ij} \xi^i, \quad V_{ij} = \binom{i}{j} h^j a^{i-j} v_i. \quad (2.3)$$

If we consider the limiting case of $h \rightarrow 0$, we then arrive at the simple boundary value problem $-F''(\xi) = \lambda F(\xi)$, $F(0) = F(\pi) = 0$ whose orthonormalized eigenfunctions can easily be found as follows:

$$\phi_m(\xi) = \sqrt{2/\pi} \sin m\xi, \quad m = 1, 2, \dots \quad (2.4)$$

So we may choose the trial function of the form

$$\psi_T(\xi) = \sum_{m=1}^{\infty} f_m \phi_m(\xi), \quad (2.5)$$

in which the f_m are the linear combination coefficients. With the application of the variational principle, we therefore obtain the matrix eigenvalue problem

$$\sum_{n=1}^{\infty} (H_{mn} - h^2 E \delta_{mn}) f_n = 0, \quad m = 1, 2, \dots, \quad (2.6)$$

where δ_{mn} is Kronecker's delta. We call H_{mn} the variational matrix which is obtained such that

$$H_{mn} = m^2 \delta_{mn} + h^2 \sum_{i=1}^{2M} \sum_{j=0}^i V_{ij} [R_{m-n}^{(j)} - R_{m+n}^{(j)}]. \quad (2.7)$$

The integrals $R_k^{(j)}$,

$$R_k^{(j)} = \frac{1}{\pi} \int_0^\pi \xi^j \cos k\xi \, d\xi \quad (2.8)$$

can be evaluated by means of integration by parts.

It is clear that a pure symmetrical problem is under investigation if the problem is defined on a symmetric interval and the potential is an even polynomial in x . In such a case we may separate the set of eigenlevels into two subsets which contain even and odd functions of x , respectively, i.e., even and odd parity states. As a symmetrical problem, we deal with the even parity states of the quartic oscillator, $V(x) = x^2 + \beta x^4$, at the numerical side of this work for the purpose of comparing computational results, especially with those of Taşeli and Demiralp [1], who have published

extremely accurate results for the infinite interval version of this problem. To this end, we use the same values of the anharmonicity constant β and take care of only the ground state energies in our numerical table. The first 10 excited state eigenvalues can be calculated without any loss of accuracy. However, results are not presented due to table economization. Therefore Table II includes ground state energies as a function of β and α , and the results taken from the Ref. [1] for $\alpha = \infty$.

We consider as a second numerical example the asymmetrical potential of the form $V(x) = v_2x^2 + v_3x^3 + v_4x^4$ which has two minima if $9v_3^2 > 32v_2v_4$. This type of oscillator is called a double-well oscillator and is of practical interest for protonic movement of hydrogen-bonded systems [22]. We solve this problem for particular potentials where $\{v_2, v_3, v_4\} = \{-7, \frac{1}{2}, 1\}$ and $\{v_2, v_3, v_4\} = \{-1, 3, 1\}$. Such potentials were considered by Somorjai and Hornig [22]. The potential $\{v_2, v_3, v_4\} = \{-7, \frac{1}{2}, 1\}$ was also investigated numerically by Killingbeck [23] and by Diaz *et al.* [24]. Numerical calculations are made for a symmetric interval $[-\alpha, \alpha]$, and results for the ground and first excited states are reported in Table III as a function of α .

3. CONCLUDING REMARKS

A rather simple and easily applicable Rayleigh-Ritz variational method has been presented to solve the Schrödinger equation with an arbitrary polynomial potential. It is deduced numerically that the usual requirement of the wavefunction vanishing at infinity may be modified. Indeed, the specimen calculations reported in this work show that it is always possible to find such an α value for which the results fit accurately to the results of $\alpha = \infty$.

It is noteworthy that in numerical computations we used quadruple precision arithmetic on a VAX-11/780 computer (34 digits) by truncating the results to 30 significant digits. The N values in numerical tables for which the corresponding eigenvalue stabilizes demonstrate the number of basis elements required. The accuracy of the results is checked by systematically increasing the dimension N , and the maximum uncertainty in the tabulated eigenvalues is ± 1 in the last figure.

One would expect that the asymptotic energy would be reached if $V(\alpha) \gg E$. The α value for which the boundedness effect on the low-lying states is less than $\epsilon = 10^{-30}$ may be called as the critical distance, say α_{cr} . That is, the low-lying state energies are equal to those of $\alpha = \infty$ within 30-digit accuracy when α tends to α_{cr} . In Table I such α_{cr} values for the quartic anharmonic oscillator are presented as a function of β .

It is clearly shown from the table that the distance α at which the asymptotic energy reached will necessarily decrease as β increases. This is due to the fact that, as β

TABLE I
The Critical Distances of α as a Function of β

β :	0	0.01	0.1	1	10	100	1000
α_{cr} :	10	10	7.5	5	3.5	2.5	1.75

increases, the wavefunction is contracted. However, we should have looked for α_{cr} values, which will be greater than the values given in Table I, for the computation of the energy states with higher quantum numbers. Therefore, the α_{cr} depends on the quantum number n , the desired accuracy for the eigenvalues ϵ , and the particular asymptotic behaviour of the potential function under consideration.

A very interesting regularity can be shown from Table II that the method is most rapidly convergent at the critical distances of α , and 30 significant figures have been obtained by using 30–35 basis elements. Since there is not a remarkable change in the number of basis elements required as β varies from 0 to 1000, we suggest that the present algorithm is extremely accurate in the whole range of β . Slowly convergent properties are observed only when $\alpha \ll \alpha_{cr}$. In

TABLE II

Ground State Eigenvalues of the Quartic Anharmonic Oscillator
 $V(x) = x^2 + \beta x^4$ for Various α , as a Function of β

β	α	N	Energy
0	1	80	2.596 919 664 064 113
	5	70	1.000 000 000 153 434 264
	10	30	1.000 000 000 000 000 000 000 000 000 00
	∞	Exact	1
0.1	1	80	2.600 911 846 801 122
	5	100	1.065 285 509 543 718 449 525 89
	7.5	30	1.065 285 509 543 717 688 857 091 628 79
	∞	Ref. [1]	1.065 285 509 543 717 688 857 091 628 79
1	1	80	2.636 580 202 486 086
	5	30	1.392 351 641 530 291 855 657 507 876 61
	10	55	1.392 351 641 530 291 855 657 507 876 61
	∞	Ref. [1]	1.392 351 641 530 291 855 657 507 876 61
10	1	130	2.969 398 036 327 419
	3.5	30	2.449 174 072 118 386 918 268 793 906 19
	5	45	2.449 174 072 118 386 918 268 793 906 19
	∞	Ref. [1]	2.449 174 072 118 386 918 268 793 906 19
100	1	160	5.014 584 738 023 400
	2.5	35	4.999 417 545 137 587 829 294 632 037 35
	5	65	4.999 417 545 137 587 829 294 632 037 35
	∞	Ref. [1]	4.999 417 545 137 587 829 294 632 037 35
1000	1	80	10.639 788 734 085 487
	1.75	35	10.639 788 711 328 046 063 622 042 669 4
	5	90	10.639 788 711 328 046 063 622 042 669 4
	∞	Ref. [1]	10.639 788 711 328 046 063 622 042 669 4

TABLE III

The Ground and the First Excited State Eigenvalues of Asymmetrical Double-Well Oscillators as a Function of α

Potential	α	n	N	Energy
$-7x^2 + \frac{1}{2}x^3 + x^4$	5	1	170	-12.258 798 853 577 533 406 063 612 270
		2	170	-6.045 687 523 772 087 327 257 502 082 4
	7.5	1	100	-12.258 798 853 577 533 406 065 133 150 7
		2	100	-6.045 687 523 772 087 327 257 522 452 00
	10	1	140	-12.258 798 853 577 533 406 065 133 150 6
		2	145	-6.045 687 523 772 087 327 257 522 451 99
$-x^2 + 3x^2 + x^4$	5	1	70	-10.619 965 590 991 627
		2	70	-4.337 045 060 252 337 65
	7.5	1	100	-10.619 965 590 991 272 864 401 501 804 8
		2	100	-4.377 045 060 252 553 938 542 258 537 99
	10	1	130	-10.619 965 590 991 272 864 401 501 804 8
		2	130	-4.377 045 060 252 553 938 542 258 537 99

such cases, eigenvalues accurate approximately to 10 digits rapidly stabilize, but if more accurate results are sought by increasing N , a dramatic slowing down of convergence occurs. So our method fails to yield the same accuracy for α values which are not in the vicinity of α_{cr} . In the other case when $\alpha \gg \alpha_{cr}$, although it is necessary to provide larger number of basis elements, the same accuracy and certainly the same results with those of $\alpha = \alpha_{cr}$ can be obtained. For this reason the estimation of α_{cr} is an important aspect of the method in order to deal with a reasonable truncation order N .

For the double-well case, we observe similarly from Table III that the eigenvalues remain almost unchanged when $\alpha \gg 7.5$. Therefore, the boundedness effect can be neglected. Because of the asymmetrical structure of the potential we cannot separate even and odd parity states, which results in using a larger number of basis elements than the symmetrical case. We may, however, state that the eigenvalues of double-well oscillators with such an accuracy have been computed for the first time.

Consequently, our method may be applied mainly for two purposes. First, we can use it to approach the energy spectrum of the usual problem defined on the open interval $(-\infty, \infty)$ by estimating its critical distance α_{cr} . Second; we can use it to solve enclosed quantum mechanical systems both for symmetrical and asymmetrical finite intervals.

Without giving an explicit table, we have shown that calculated results for bounded harmonic oscillator improve those of the other works [11, 12, 15], but agree to the first few digits. Another important feature of this method is the applicability of an arbitrary polynomial oscillator. Only two examples, however, are given here, in order not to overfill the content of the paper with tabular material anymore. Further results for some interesting potentials will be reported in due course. For instance, the symmetrical two-well oscillator $V(x) = -x^2 + \beta x^4$ and the symmetrical three-well oscillator $V(x) = v_2 x^2 - v_4 x^4 + v_6 x^6$, where $v_4^2 \geq 4v_2 v_6$, are presently under investigation.

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