

---

# Accurate Lower and Upper Bounds of the Energy Spectrum for the Asymmetrical Two-Well Potentials

---

H. TAŞELI

*Department of Mathematics, Middle East Technical University, 06531 Ankara, Turkey*

*Received September 20, 1995; accepted October 19, 1995*

## ABSTRACT

---

Trigonometric basis sets are used in a Rayleigh–Ritz variational method for computing two-sided eigenvalue bounds of the Schrödinger equation in one dimension. The method is based on truncating the infinite interval and solving an eigenvalue problem which obeys the von Neumann and the Dirichlet boundary conditions, respectively. Highly accurate numerical results are presented for the asymmetrical two-well oscillators.

© 1996 John Wiley & Sons, Inc.

---

## 1. Introduction

In a recent article [1], Taşeli presented an efficient technique for solving the Schrödinger equation:

$$-\Psi''(x) + V(x)\Psi(x) = E\Psi(x), \quad x \in (-\infty, \infty), \quad (1.1)$$

where  $V(x)$  is a symmetrical, i.e.,  $V(-x) = V(x)$ , a multiminima potential. The approximation assumes a truncated symmetric interval  $[-\alpha, \alpha]$  and utilizes simple trigonometric basis functions in the variational method. More recently, Zitnan [2] modified the trigonometric functions given in [1] and proposed an extended Rayleigh–Ritz method with a B-spline approximation to calculate lower and

upper bounds of the eigenvalues  $E$  of (1.1). In his work [2], Zitnan found the accuracy of Taşeli's approach very impressive with the reservation that it suffers from the lack of error estimates.

In this study, we deduce that the simple trigonometric functions may be employed to compute lower bounds of the energy spectrum of (1.1) as well as the usual upper bounds yielded by the Rayleigh–Ritz method. At the same time, the present article is a completion of [1] which shows that the method therein can also be applied to the asymmetrical problems, with a natural modification. Therefore, we consider a general polynomial potential

$$V(x) = \sum_{i=1}^M v_i x^i \quad (1.2)$$

containing both odd and even powers of  $x$ , where

the  $v_i$  are the coupling constants. As a specific example, we solve the asymmetrical Schrödinger equation with

$$V(x) = v_2 x^2 + v_3 x^3 + v_4 x^4, \quad (1.3)$$

which is a double-well potential if the parameters satisfy the inequalities

$$v_4 > 0, \quad 9v_3^2 - 32v_2v_4 > 0. \quad (1.4)$$

Note that the absence of the linear term,  $v_1 x$ , in (1.3) does not cause any loss of generality since it can always be removed by shifting the coordinate axis.

This type of oscillator is of practical interest for the protonic movement of hydrogen-bonded systems [3]. It was considered numerically by Diaz et al. [4]. Znojil [5] constructed Hill's determinant of the problem by matching two suitable power series valid for  $x < 0$  and  $x > 0$ , respectively. However, a systematic investigation of the energy spectrum over a wide range of the coupling constants is not available in the literature.

This article is organized as follows: Section 2 enlightens the theoretical background of determining error bounds for the eigenvalues when the Schrödinger equation is defined on a finite interval. Section 3 presents the trigonometric basis sets appropriate to the boundary conditions of the Dirichlet and von Neumann types. The last section contains the numerical results and the concluding remarks as usual.

## 2. Lower and Upper Bounds for the Eigenvalues

Whenever Eq. (1.1) is reconsidered over the truncated domain of  $x \in [-\alpha, \beta]$ , the usual wave function  $\Psi^{(\infty)}(x)$  and the eigenvalues  $E^{(\infty)}$  may formally be written as

$$\Psi = \Psi(x; \alpha, \beta), \quad \lim_{\alpha, \beta \rightarrow \infty} \Psi(x; \alpha, \beta) = \Psi^{(\infty)}(x) \quad (2.1)$$

and

$$E = E(\alpha, \beta), \quad \lim_{\alpha, \beta \rightarrow \infty} E(\alpha, \beta) = E^{(\infty)}, \quad (2.2)$$

where the positive constants  $\alpha$  and  $\beta$  are the boundary parameters. Thus, the wave function can be regarded as a function of several variables

satisfying the condition

$$A\Psi(x; \alpha, \beta) + B\Psi_x(x; \alpha, \beta) = 0 \quad (2.3)$$

at  $x = -\alpha$  and  $x = \beta$ , where the subscript  $x$  denotes partial derivative with respect to  $x$ . The constants  $A$  and  $B$  in (2.3) are either zero or unity so that a von Neumann or a Dirichlet boundary value problem is under discussion according to that  $A$  or  $B$  is equal to zero.

Now, the differentiation of (1.1) with respect to  $\alpha$  gives the equation

$$\mathcal{L}\Psi_\alpha = E_\alpha\Psi, \quad \mathcal{L} = -\frac{\partial^2}{\partial x^2} + V(x) - E, \quad (2.4)$$

from which, on multiplying by  $\Psi$  and integrating from  $-\alpha$  to  $\beta$ , it follows that

$$\langle \Psi, \Psi \rangle E_\alpha = \langle \mathcal{L}\Psi_\alpha, \Psi \rangle. \quad (2.5)$$

Here, subscripts denote again partial derivatives, and the ket and bra notation implies the inner product defined by the integral operation over the domain of  $x$ . We may assume that the wave function is normalized and, after integration by parts, write (2.5) in the form

$$E_\alpha = \text{boundary terms} + \langle \Psi_\alpha, \mathcal{L}^*\Psi \rangle. \quad (2.6)$$

Since the operator  $\mathcal{L}$  is formally self-adjoint, i.e.,  $\mathcal{L}^* = \mathcal{L}$ , the inner product in (2.6) vanishes from (1.1). We, therefore, have the result

$$E_\alpha \equiv \frac{\partial E}{\partial \alpha} = [\Psi_x(x; \alpha, \beta)\Psi_\alpha(x; \alpha, \beta) - \Psi(x; \alpha, \beta)\Psi_{\alpha x}(x; \alpha, \beta)] \Big|_{x=-\alpha}^{\beta}. \quad (2.7)$$

The use of boundary conditions gives the possibility of expressing Eq. (2.7) in a more appropriate form. To this end, let us consider the total differential of a function of three independent variables,  $F = F(x, \alpha, \beta)$  say:

$$dF = F_x dx + F_\alpha d\alpha + F_\beta d\beta. \quad (2.8)$$

However, if  $x$  is a function of  $\alpha$ , for instance,  $x = -\alpha$ , then  $dx = -d\alpha$  and, hence,

$$dF = (F_\alpha - F_x) d\alpha + F_\beta d\beta. \quad (2.9)$$

In this case, the partial derivative of such a function with respect to  $\alpha$  is clearly equal to  $F_\alpha - F_x$ . Therefore, the partial differentiation of the bound-

ary conditions in (2.3) with respect to  $\alpha$  yields the relations

$$A[\Psi_{\alpha}(-\alpha; \alpha, \beta) - \Psi_x(-\alpha; \alpha, \beta)] + B[\Psi_{\alpha x}(-\alpha; \alpha, \beta) - \Psi_{xx}(-\alpha; \alpha, \beta)] = 0 \quad (2.10)$$

and

$$A\Psi_{\alpha}(\beta; \alpha, \beta) + B\Psi_{\alpha x}(\beta; \alpha, \beta) = 0. \quad (2.11)$$

Substituting (2.10) and (2.11) into (2.7) and using Eqs. (1.1) and (2.3), we finally obtain

$$\frac{\partial E}{\partial \alpha} = -\Psi_x^2(-\alpha; \alpha, \beta) + [V(-\alpha) - E(\alpha, \beta)]\Psi^2(-\alpha; \alpha, \beta). \quad (2.12)$$

The same procedure may be repeated for the other boundary parameter  $\beta$  to find

$$\frac{\partial E}{\partial \beta} = -\Psi_x^2(\beta; \alpha, \beta) = [V(\beta) - E(\alpha, \beta)]\Psi^2(\beta; \alpha, \beta). \quad (2.13)$$

As a result, if the problem being considered obeys Dirichlet boundary conditions, i.e.,

$$\Psi(-\alpha; \alpha, \beta) = \Psi(\beta; \alpha, \beta) = 0, \quad (2.14)$$

then (2.12) and (2.13) reduce to

$$\frac{\partial E}{\partial \alpha} = -\Psi_x^2(-\alpha; \alpha, \beta), \quad \frac{\partial E}{\partial \beta} = -\Psi_x^2(\beta; \alpha, \beta), \quad (2.15)$$

showing that  $E(\alpha, \beta)$  decreases monotonically to its limit  $E^{(\infty)}$  as  $\alpha$  and  $\beta$  increase. This is the well-known property which implies that the eigenvalues of (1.1) satisfying Dirichlet boundary conditions (2.14) are upper bounds for the exact asymptotic eigenvalues.

Conversely, the von Neumann boundary value problem assumes that

$$\Psi_x(-\alpha; \alpha, \beta) = \Psi_x(\beta; \alpha, \beta) = 0 \quad (2.16)$$

and, hence, that Eqs. (2.12) and (2.13) take the form

$$\frac{\partial E}{\partial \alpha} = [V(-\alpha) - E(\alpha, \beta)]\Psi^2(-\alpha; \alpha, \beta), \quad \frac{\partial E}{\partial \beta} = [V(\beta) - E(\alpha, \beta)]\Psi^2(\beta; \alpha, \beta). \quad (2.17)$$

These relations suggest evidently that the eigenvalues obtained by means of the von Neumann boundary value problem are lower bounds since they increase monotonically to  $E^{(\infty)}$  as  $\alpha$  and  $\beta$  increase, provided that

$$V(-\alpha) > E(\alpha, \beta), \quad V(\beta) > E(\alpha, \beta). \quad (2.18)$$

In other words,  $-\alpha$  and  $\beta$  must lie beyond the classical turning points to this end. It is worth mentioning that similar results were deduced by Fernandez and Castro in another context [6].

Consequently, the problem now turns out to solve Eq. (1.1) subject to both Dirichlet and von Neumann boundary conditions, which provide us with a practical method of determining upper and lower bounds, respectively, for the unbounded eigenvalues required.

### 3. Trigonometric Basis Sets

We generate normalized basis functions by considering the unperturbed Schrödinger equation taken to be of the form

$$-\frac{d^2\Psi}{dx^2} = \lambda^2\Psi, \quad x \in [-\alpha, \beta], \quad (3.1)$$

in which a rectangular well potential, i.e.,

$$V(x) = \begin{cases} \infty, & x \leq -\alpha \\ 0, & -\alpha < x < \beta \\ \infty, & x \geq \beta \end{cases} \quad (3.2)$$

is assumed. In [1], the trigonometric basis sets were derived by employing a similar problem defined necessarily on a symmetric interval  $x \in [-\alpha, \alpha]$  which yields even and odd trial solutions, separately. Owing to the asymmetric structure of the potentials concerned with in this study, however, we cannot decompose the set of eigenlevels into two subsets representing, independently, the symmetric and antisymmetric levels. Fortunately, the mapping of the domain from  $x \in [-\alpha, \beta]$  to  $\xi \in [0, \pi]$ , where

$$\xi = \frac{\pi}{\alpha + \beta}(x + \alpha), \quad (3.3)$$

simplifies the eigensolutions of (3.1) and reflects

successfully the asymmetric character of the problem for any choice of  $\alpha$  and  $\beta$  even if  $\alpha = \beta$ . Therefore, integrating Eq. (3.1) in the transformed interval accompanying with the boundary conditions

$$\Psi(0) = \Psi(\pi) = 0, \quad \Psi'(0) = \Psi'(\pi) = 0 \quad (3.4)$$

individually, we obtain

$$\phi_k^{(U)}(\xi) = \sqrt{\frac{2}{\pi}} \sin k\xi, \quad k = 1, 2, \dots \quad (3.5)$$

and

$$\begin{aligned} \phi_1^{(L)}(\xi) &= \frac{1}{\sqrt{\pi}}, \\ \phi_k^{(L)}(\xi) &= \sqrt{\frac{2}{\pi}} \cos(k-1)\xi, \quad k = 2, 3, \dots \end{aligned} \quad (3.6)$$

As is readily seen, the  $\phi_k^{(U)}(\xi)$  and  $\phi_k^{(L)}(\xi)$  stand for the solutions satisfying, respectively, the Dirichlet- and von Neumann-type boundary value problems. It should be noticed that we have only one admissible sequence of eigenfunctions in each case. Furthermore, both  $\{\phi_k^{(U)}(\xi)\}$  and  $\{\phi_k^{(L)}(\xi)\}$  form complete orthonormal sets for  $\xi \in [0, \pi]$ , i.e.,

$$\langle \phi_k^{(U)}, \phi_m^{(U)} \rangle = \delta_{km}, \quad \langle \phi_k^{(L)}, \phi_m^{(L)} \rangle = \delta_{km}, \quad k, m = 1, 2, \dots, \quad (3.7)$$

where  $\delta_{km}$  is the Kronecker delta.

Now, the theoretical results in Section 2 imply the use of the trial functions

$$\Psi^{(U)}(\xi) = \sum_{k=1}^{\infty} f_k \phi_k^{(U)}(\xi) \quad (3.8)$$

and

$$\Psi^{(L)}(\xi) = \sum_{k=1}^{\infty} g_k \phi_k^{(L)}(\xi) \quad (3.9)$$

in calculating upper and lower bounds eigenvalues of the full Schrödinger equation, respectively, where the  $f_k$  and  $g_k$  are the linear combination coefficients. By the change of variable (3.3), the Schrödinger equation is unaltered in the form

$$\begin{aligned} \left[ -\frac{d^2}{d\xi^2} + l^2 V(\xi) \right] \Psi(\xi) &= l^2 E \Psi(\xi), \\ l &= \frac{\alpha + \beta}{\pi}, \quad \xi \in [0, \pi], \end{aligned} \quad (3.10)$$

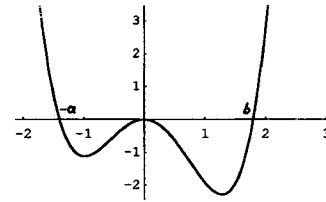


FIGURE 1. Asymmetrical two-well oscillators:  $v_2 < 0$ .

with the potential replaced by

$$V(\xi) = \sum_{i=1}^M \sum_{j=0}^i a_{ij} \xi^j, \quad a_{ij} = v_i \binom{i}{j} l^j (-\alpha)^{i-j}, \quad (3.11)$$

where  $l$  denotes the length of the original interval divided by  $\pi$ .

Making use of expansions (3.8) and (3.9) for the wave function, the differential equation in (3.10) is reduced to two standard matrix eigenvalue problems. More specifically, if we take the Dirichlet-type solution  $\Psi^{(U)}(\xi)$ , we then find that

$$\sum_{k=1}^{\infty} [H_{mk}^{(U)} - l^2 E \delta_{mk}] f_k = 0, \quad m = 1, 2, \dots, \quad (3.12)$$

where the variational matrix  $H_{mk}^{(U)}$  is given by

$$H_{mk}^{(U)} = m^2 \delta_{mk} + l^2 \sum_{i=1}^M \sum_{j=0}^i a_{ij} [R_{m-k}^{(j)} - R_{m+k}^{(j)}]. \quad (3.13)$$

By the von Neumann-type solution  $\Psi^{(L)}(\xi)$ , on the other hand, we have

$$\sum_{k=1}^{\infty} [H_{mk}^{(L)} - l^2 E \delta_{mk}] g_k = 0, \quad m = 1, 2, \dots, \quad (3.14)$$

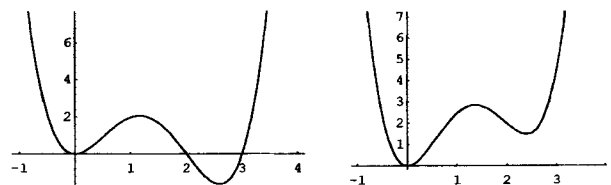


FIGURE 2. Asymmetrical two-well oscillators:  $v_2 > 0$  and  $v_3 < 0$ .

with the coefficient matrix  $H_{mk}^{(L)}$  which is expressible as

$$\begin{aligned}
 H_{mk}^{(L)} &= (m-1)^2 \delta_{mk} + l^2 \left[ 1 + \left( \frac{1}{\sqrt{2}} - 1 \right) \delta_{m1} \right] \\
 &\times \left[ 1 + \left( \frac{1}{\sqrt{2}} - 1 \right) \delta_{k1} \right] \\
 &\times \sum_{i=1}^M \sum_{j=0}^i a_{ij} [R_{m+k-2}^{(j)} + R_{m-k}^{(j)}]. \quad (3.15)
 \end{aligned}$$

Note that matrix elements can be evaluated analytically in terms of the  $R_p^{(j)}$  defined by the simple integral

$$\begin{aligned}
 R_p^{(j)} &= \frac{1}{\pi} \int_0^\pi \xi^j \cos p\xi \, d\xi, \\
 j &= 0, 1, \dots; \quad p = 0, \mp 1, \mp 2, \dots \quad (3.16)
 \end{aligned}$$

having the property that  $R_{-p}^{(j)} = R_p^{(j)}$ , which implies immediately the symmetry of each matrix. Integrating by parts it follows that

$$\begin{aligned}
 R_p^{(j)} &= j! \pi^j \sum_{k=0}^{[j]} \frac{[\delta_{2k, j-1} - (-1)^k]}{(j-2k-1)!} \left( -\frac{1}{\pi^2 p^2} \right)^{k+1}, \\
 R_0^{(j)} &= \frac{\pi^j}{j+1}, \quad R_p^{(0)} = \delta_{p0}, \quad (3.17)
 \end{aligned}$$

where  $[j] = (j-1)/2$  or  $(j-2)/2$  according as  $j$  is odd or even. A recursion relation of the form

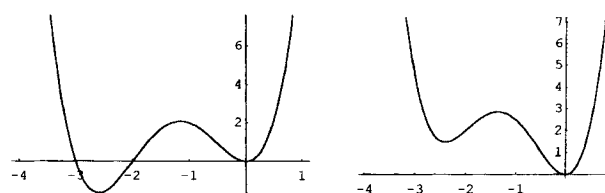


FIGURE 3. Asymmetrical two-well oscillators:  $v_2 > 0$  and  $v_3 > 0$ .

may also be introduced:

$$p^2 R_p^{(j)} = j\pi^{j-2} [(-1)^p - \delta_{1j}] - j(j-1) R_p^{(j-2)}, \quad j = 1, 2, \dots \quad (3.18)$$

for any  $p \neq 0$  with the initial conditions  $R_p^{(-1)} = R_p^{(0)} = 0$ .

From a computational viewpoint, if the secular equations in (3.12) and (3.13) are truncated to finite-dimensional,  $N$  say, linear systems the roots of their characteristic equations then yield the upper- and lower-bound eigenvalues  $E^{(U)}$  and  $E^{(L)}$ , respectively. In this way, we provide error estimates in the sense that

$$E^{(L)} < E^{(\infty)} < E^{(U)}, \quad (3.19)$$

to any desired accuracy, for the asymptotic eigenvalues  $E^{(\infty)}$  by systematically increasing the

TABLE I  
Lower and upper bounds to eigenvalues  $\lambda_n$  of asymmetrical double-well oscillators for  $c_1 = 0.01$ , as a function of  $c_2$ .

$c_2$	$\alpha$	$N$	$n$	$\lambda_n$
0.25	10	50	0	0.2204969335513831811805841 / 42
			1	0.7990761561340410427563358 / 59
			2	1.5794258727150421868397882 / 83
			3	2.4752271262769579979403548 / 56
0.50	10	50	0	0.2182555367970654073539824 / 25
			1	0.7934758524493513007184669 / 70
			2	1.5717267991669847515874491 / 92
			3	2.4655965377851385748576954 / 57
0.75	10	50	0	0.2152072540479717488436246 / 47
			1	1.7858678700085982553313958 / 59
			2	1.5612866356953751107760212 / 13
			3	2.4525427214641787638060918 / 19

**TABLE II**  
Lower and upper bounds to eigenvalues  $\lambda_n$  of asymmetrical double-well oscillators for  $c_1 = 1$ , as a function of  $c_2$ .

$c_2$	$\alpha$	$N$	$n$	$\lambda_n$
0.25	4.75	52	0	0.8696946176473187733457090 / 91
			1	3.3587938284332880537010484 / 85
			2	6.8590731620561962332569335 / 44
			3	10.903704068138317871260595 / 604
0.50	4.75	52	0	0.8201545100282241864518350 / 51
			1	3.2344141263192277422940691 / 92
			2	6.6911502752955136276965453 / 54
			3	10.694056898461014997542819 / 21
0.75	4.75	52	0	0.7523137482182902265081869 / 70
			1	3.0623718040642200853199345 / 46
			2	6.4616818177088380466913991 / 92
			3	10.408002113532361485956111 / 12

truncation size  $N$  and the boundary parameters  $\alpha$  and  $\beta$ .

#### 4. Results and Discussion

The present method is applied to the asymmetrical two-well potentials (1.3) as indicated previously in the Introduction. The necessary and sufficient conditions to deal with a double-well oscillator are given by (1.4). An additional inspection on such a polynomial of degree four shows that it possesses two real roots of opposite signs if  $v_2 < 0$ , except the double root at  $x = 0$ . Thus, two negative valued minima located asymmetrically

about the origin appear to be independent of  $v_3$  (Fig. 1). The deeper well occurs along the positive real axis when  $v_3 < 0$  and vice versa. In this case of  $v_2 < 0$ , we have a local maximum at  $x = 0$ .

If  $v_2 > 0$ , one minimum then appears at the origin, and the locations of the other extrema depend upon  $v_3$  (Figs. 2 and 3). These potentials have two nonzero real roots whenever  $v_3^2 > 4v_2v_4$ . By translating appropriately the origin of the coordinate system, however, the oscillators of the shapes illustrated by Figures 2 and 3 can be viewed as a member of the family sketched in Figure 1. Hence, without any loss of generality, the eigenvalue calculations are carried out only for the asymmetrical problems in which  $v_2 < 0$ .

**TABLE III**  
Lower and upper bounds to eigenvalues  $\lambda_n$  of asymmetrical double-well oscillators for  $c_1 = 100$ , as a function of  $c_2$ .

$c_2$	$\alpha$	$N$	$n$	$\lambda_n$
0.25	2.5	65	0	-4.2773448491824741668473488 / 87
			1	7.0805173913641586560907103 / 04
			2	19.817761502618821399175325 / 26
			3	36.209337296287706584558242 / 44
0.50	2.5	65	0	-6.8160520475367369825614305 / 04
			1	4.6756939305582900579971358 / 59
			2	15.973204136317836561600922 / 23
			3	31.505546630519551260800075 / 76
0.75	2.5	65	0	-9.4594792122245128585465626 / 25
			1	0.0105600727176196213798013 / 14
			2	10.866977233476768562653506 / 07
			3	24.888991175519381797134001 / 02

**TABLE IV**  
Lower and upper bounds to eigenvalues  $\lambda_n$  of asymmetrical double-well oscillators for  $c_1 = 10000$ , as a function of  $c_2$ .

$c_2$	$\alpha$	$N$	$n$	$\lambda_n$
0.25	1.4	90	0	-1296.408751695166249416336 / 35
			1	-1074.567775210872886170689 / 88
			2	-861.8866820289173763017492 / 91
			3	-659.5154356829335920393668 / 67
0.50	1.4	90	0	-1647.930675290045502028518 / 17
			1	-1407.017125267978036042450 / 49
			2	-1174.069091277533492714275 / 74
			3	-949.8921122676190060284722 / 21
0.75	1.4	90	0	-2002.685368625287806885737 / 36
			1	-1743.496266574938498655389 / 88
			2	-1491.483476175760688786027 / 26
			3	-1247.271556935708503649640 / 39

The potential (1.3) with  $v_2 < 0$  (Fig. 1) is best characterized by the equation

$$V(x) = v_4 x^2(x + a)(x - b), \quad (4.1)$$

where  $a$  and  $b$  are positive parameters. Assuming that  $b > a$ ,  $V(x)$  can be written as

$$V(x) = b^4 v_4 \left(\frac{x}{b}\right)^2 \left(\frac{x}{b} + \frac{a}{b}\right) \left(\frac{x}{b} - 1\right), \quad (4.2)$$

which implies transforming the variable from  $x$  to  $x/b$ . Therefore, the Schrödinger equation takes the form

$$\left[ -\frac{d^2}{dx^2} + c_1 x^2(x + c_2)(x - 1) \right] \Psi(x) = \lambda \Psi(x), \quad (4.3)$$

**TABLE V**  
The rate of convergence of the method as a function of  $\alpha$ , where  $V(x) = 0.01x^2(x + 0.25)(x - 1)$ .

$\alpha$	$N$	$\lambda_0$
4	10	0.20 / 23
5	12	0.22021 / 73
6	15	0.2204959 / 79
7	18	0.22049693320 / 88
8	26	0.220496933551375 / 91
9	36	0.22049693355138318117 / 19
10	50	0.220496933551383181180584100 / 02
11	56	0.22049693355138318118058410122 / 23

where

$$c_1 = b^6 v_4, \quad c_2 = \frac{a}{b}, \quad \lambda = b^2 E. \quad (4.4)$$

Now, the rescaled equation contains only two eigenvalue parameters  $c_1$  and  $c_2$  such that

$$c_1 > 0, \quad 0 < c_2 < 1, \quad (4.5)$$

giving the possibility of the systematic investigation of the problem in a concise manner. We may return back to the original coupling constants by using the relationships

$$v_2 = -c_1 c_2 b^{-4}, \quad v_3 = -c_1(1 - c_2)b^{-5}, \quad v_4 = c_1 b^{-6}, \quad (4.6)$$

where the absolutely greater root  $b$  of the potential remains as a free parameter. Note also that if  $b < a$  then we are confronted with a potential which can be obtained by interchanging the two wells in Figure 1. As a results, there is no need to consider such an eigenvalue problem since its spectrum is obviously equivalent to that expressed by Eq. (4.3), in any symmetrical interval of  $x$ .

Within this formalism, the infinite interval of  $x$ ,  $x \in (-\infty, \infty)$ , is approximated by the finite one,  $x \in [-\alpha, \alpha]$ , setting  $\beta = \alpha$ , which imitates the symmetry of the domain. The numerical results are reported in Tables I-IV for  $c_1$  values of 0.01, 1, 100, and 10000 respectively, as a function of  $c_2$ . The range of  $c_2$  is covered by choosing  $c_2 = 0.25, 0.5, \text{ and } 0.75$ . It is clear that the left-hand limiting value of  $c_2, c_2 = 0$ , does not represent a double-well oscillator anymore where the potential has an

inflection point at  $x = 0$ . On the other hand,  $c_2 = 1$  corresponds to a symmetrical two-well potential which was examined extensively in [1]. The last table (Table V) demonstrates the rate of convergence of the method in calculating error bounds for a specimen problem as the boundary parameter  $\alpha$  varies.

In the tables,  $n$  is the state number, and  $N$  stands for the number of basis functions required to get the recorded accuracy. The energy eigenvalues are tabulated according to Zitnan's [2] notation. For instance, 0.22021/73 in Table V denotes two-sided eigenvalue bounds such that

$$0.22021 \leq \lambda_0 \leq 0.22073, \quad (4.7)$$

where the lower bounds are truncated and the upper bounds are rounded up. An inverse procedure is adopted for negative eigenvalues. We notice from the listed energy eigenvalues that they are correct up to more than 20 digits. Furthermore, Table V implies evidently that the accuracy of the results may, step by step, be improved depending on the machine accuracy.

The basis sets described in this work to determine lower- and upper-bound eigenvalues lead to

very rapidly converging algorithms with almost the same rate. Consequently, we have shown, both analytically and numerically, that such simple trigonometric functions can be used effectively in solving asymmetrical problems as well. The results presented with this high degree of precision may be regarded as a guide to future numerical calculations. Moreover, it is straightforward to extend the method to two-dimensional Schrödinger equation with asymmetrical potentials, as was done for the symmetrical problems [7].

---

## References

1. H. Taşeli, *Int. J. Quantum Chem.* **46**, 319 (1993).
2. P. Zitnan, *Int. J. Quantum Chem.* **52**, 1267 (1994).
3. R. L. Somorjai and D. F. Hornig, *J. Chem. Phys.* **36**, 1980 (1962).
4. C. G. Diaz, F. M. Fernandez, and E. A. Castro, *J. Phys. A: Math. Gen.* **21**, L11 (1988).
5. M. Znojil, *J. Math. Phys.* **33**, 213 (1992).
6. F. M. Fernandez and E. A. Castro, *Int. J. Quantum Chem.* **19**, 521 (1981).
7. H. Taşeli and R. Eid, *Int. J. Quantum Chem.* **59**, 183 (1996).