Energy eigenvalues for free and confined triple-well potentials

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Some confined and unconfined (free) one–dimensional triple–well potentials are analyzed with two different numerical approaches. Confinement is achieved by enclosing the potential between two impenetrable walls. The unconfined (free) system is recovered as the positions of the walls move to infinity. The numerical solutions of the Schrödinger equation for the symmetric and asymmetric potentials without confinement, are comparable in precision with those obtained anaylitically. For the symmetric triple–well potentials, $V(x) = \alpha x^2 - \beta x^4 + x^6$, it is found that there are sets of two or three quasi-degenerate eigenvalues depending on the parameters α and β. A heuristic analysis shows that if the conditions $\alpha = (\beta^2/4) \pm 1$ (with $\alpha > 0$ and $\beta > 0$) are satisfied, then there are sets of three eigenvalues with similar energy. An interesting behavior is found when one impenetrable wall is fixed and the other is moved to different positions. In summary, the number of local minima that the potential has in the confined region determines a two- or three-fold degeneracy.

Keywords: One–dimensional triple–well potentials; energy eigenvalues and eigenfunctions; confined quantum systems.

Analizamos algunos potenciales unidimensionales de triple pozo, libres y confinados, mediante dos métodos numéricos. El confinamiento se realiza encajonando al potencial entre dos paredes impenetrables. El sistema libre se recobra cuando las posiciones de las paredes se mueven a infinito. Las soluciones de la ecuación de Schrödinger, para estos potenciales simétricos y asimétricos libres de confinamiento, que se obtienen mediante los métodos numéricos de este trabajo son comparables en presición con los resultados analíticos. Para potenciales simétricos de triple pozo, $V(x) = \alpha x^2 - \beta x^4 + x^6$, se encuentran conjuntos de dos o tres valores propios casi degenerados dependiéndo de los valores de α y β. Un análisis heurístico muestra que si las condiciones $\alpha = (\beta^2/4) \pm 1$ (con $\alpha > 0$ y $\beta > 0$) se satisfacen, entonces habrá un conjunto de tres valores propios con energía similar. Se encuentra un comportamiento interesante cuando una de las paredes se mantiene fija y la otra se mueve a diferentes posiciones. El número de mínimos locales que tiene el potencial en la región de confinamiento determina una degeneración doble o triple

Descriptores: Potenciales unidimensionales con triple pozo; energías y funciones propias; sistemas cuánticos confinados.

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1. Introduction

Undoubtedly, the harmonic oscillator is a cornerstone in Physics with broad implications and applications in so many branches of Science that its impact is a well known fact even to non-experts. Its simplicity allows an analysis that highlights the important underlying physical reasons behind many problems in Physics, Chemistry and Biology. However, since the harmonic approximation is in general the first term in the expansion of a harmonic potential near a local minimum, to gain further insight about many problems it is mandatory to go beyond and include a harmonic corrections. Paradigmatic examples of anharmonic potentials are the symmetric and non-symmetric triple wells, which are useful models in condensed matter applications to study photoluminescence, the blue shift induced by the annealing in GaNAs/GaAs, the spin-selective positioning of wave functions, just to mention a few [1-9]. In some of these and other problems, spatial confinement plays a crucial role and, consequently, a model that incorporates this restriction will contribute to a better understanding of the interplay between anharmonicity and confinement.

The most general one–dimensional anharmonic potential of polynomial kind can be represented as

$$V(x) = \sum_{n=1}^{M} b_n x^n, \qquad -\infty < x < \infty \tag{1}$$

with M an even integer, and where the b_0 term is omitted because it is only an additive constant. There are several stud-

ies [10-22] devoted to the solution of the Schrödinger equation for the one–dimensional symmetric double–well potential, considerably less regarding the symmetric triple-well, and very few have focused on the non–symmetric double-well.

Several methods have been developed to study symmetric potentials for $M > 1$. Some of them are: semiclassical methods [12,28,30], Rayleigh-Schrödinger (RS) perturbation theory [20,25,27,29], Hill determinant [19,26], linear variational method [10,11,14,17,18,22], Rayleigh-Ritz variational method [15,16,24], asymptotic series [13], Bogoliuvov transformations [21], among others [23,31,32].

There are only few examples of anharmonic potentials with exact analytical solutions [19], and in a general situation it is necessary to use an approximate technique, analytical or numerical, to solve the Schrödinger equation. The most common approach to study the one–dimensional triple–well potential is perturbation theory, even though it is well known that sometimes this approach does not converge [23]. This has led to some discrepancies between different solutions reported in the literature for the triple-well potential, strongly encouraging the use of more reliable methods to solve this interesting problem.

Recently, the authors of this work have developed two different numerical approaches to solve the one–dimensional Schrödinger equation with Dirichlet boundary conditions (DBC), allowing the reliable treatment of the so-called confined quantum systems in one–dimension. One of these methods is based on Numerov's discretization [32] and the other relies on the the Runge–Kutta (RK) integration of the differential equation [34-36]. Both methods have shown their capabilities to solve confined one–dimensional problems dealing with the Schrödinger equation for different potentials [34-36], and even to study confined many-electron atoms [33].

The aim of the present work is to study symmetrical and non-symmetrical triple–well potentials in different confining situations, including the free or unconfined case, and using the two methods mentioned in the previous lines to solve the one–dimensional Schrödinger equation for this combination of potential and boundary conditions.

The organization of this work is as follows: In Sec. 2 the methodology is briefly described. The results for free (unconfined) and confined triple–well potentials and its discussion is presented in Sec. 3. Finally, the conclusions are given in Sec. 4.

TABLE I. The ground state and the first nine excited state energies for three-well potentials. The exact values were obtained by using supersymmetric quantum mechanics and are taken from Ref. 19. Here a and b represent the positions of the infinite walls.

$V_1(x) = x^2 - 4x^4 + x^6, \quad (a = -3.8,\, b = 3.8)$		
Present	Reference [19]	Exact [19]
-2.000000000000000000000000000	-1.999 999	-2
-1.772726698991350330450917237 49	-1.772 725	
2.078279891768595361369537996 01	2.078 281	
5.604028342382013654490407549 98	5.504 034	
9.951442255544785266269000592 21		
15.246288691683715975202127422 17		
21.297054421266731218156632754 93		
28.026283505452539123020621356 58		
35.386845462393084654270406867 93		
43.338769941723050978102198168 25		
$V_2(x) = 4x^2 - 6x^4 + x^6, \qquad (a = -4.0,\, b = 4.0)$		
Present	Reference [19]	Exact [19]
-9.001720238527719715836587962 88	-9.001 244	
-9.000000000000000000000000000	-8.999 758	-9
0.639394262865333280439586675 49	0.639 810	
1.936629224926380607272063696 39	1.937 489	
4.696413325084902081900374010 82		
9.096931711179911489145971454 54		
14.031494589168474326843231325 59		
19.651503285173633283315860932 01		
25.939708830464413185529811558 27		
32.831023250752826472127043345 51		

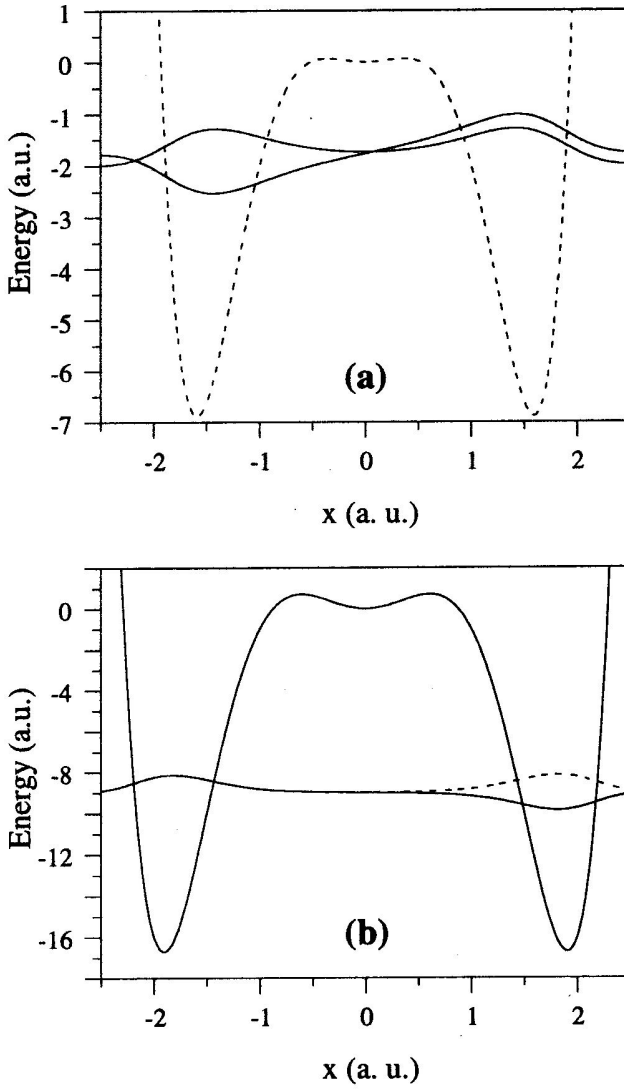

FIGURE 1. In Figures 1(a) and 1(b) we plot the ground state and the first excited state for the symmetric potencials V1(x) and V2(x), respectively. The horizontal lines represent its energy eigenvalues. In these potencials these states are almost degenerate.

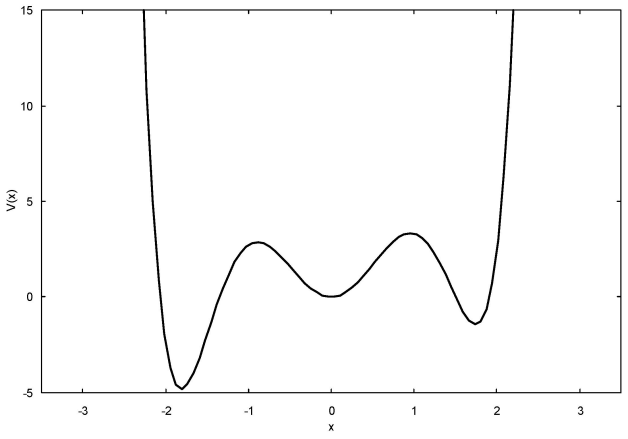

FIGURE 2. Plot of the asymmetric potential $V_4(x) = 8x^2 + 0.3x^3 - 6x^4 + x^6$.

TABLE II. Energy eigenvalues for the potential $V_3(x)$=$224x^2 - 30x^4 + x^6$. This table shows few different triplet states contained in this triple well potential. All figures are significant. To obtain this precision Method I was used with the UBASIC software and 40 figures in floating point variables. Here the position of the infinite walls are $a = -5.4$ and $b = 5.4$, respectively.

state n	Energy
1	14.865142639869404974664258699316
2	14.865142639869404974664415093047
3	14.865142639869404974664571486779
4	44.388850779725923528814763346457
5	73.493285567721654092365670334284
6	73.493285567721654093042351890314
7	73.493285567721654093719033446345
8	102.165649441285255955070801984071
9	130.391936872438506833916064513823
10	130.391936872438507604578273044361
11	130.391936872438508375240481574900
12	158.156735114528082345504829055516
13	185.442976187872563130147199467468
14	185.442976187872972479297372722890
15	185.442976187873381828447546015417
16	212.231623705625027861106650387636

2. Methodology

The numerical approaches used in this work solve efficiently the one–dimensional (1–D) Schrödinger equation. In units where $\hbar = m = 1$, the 1–D Schrödinger equation can be written as

$$-\frac{d^2\psi}{dx^2} + U(x)\psi = \epsilon\psi, \tag{2}$$

with $U(x)$ defined as

$$U(x) = \begin{cases} V(x), & \text{if } a < x < b; \\ +\infty, & \text{if } x \leq a \text{ or } x \geq b, \end{cases} , \tag{3}$$

where $V(x)$ is given by Eq. (1). By imposing the DBC, the solutions of the Schrödinger equation (2) are different from zero only in the interval (a, b). At the boundaries, the wave function takes the following values:

$$\psi(a) = 0, \quad \psi(b) = 0. \tag{4}$$

As it was mentioned above, to gain confidence on the results, two different numerical approaches are used to solve the confined problem. The first is based on the numerical integration of the differential equation by the Runge–Kutta method of order 6–8 with an adaptive integration step to get the desired accuracy [34-36], that hereafter will be referred as Method I. In this approach it is supposed that the wave function depends explicitly on the position and the energy. We solve the Schrödinger equation and an auxiliar equation, its

partial derivative respect to the energy, simultaneously. Then we use the shooting method and the Newton-Raphsom algorithm to obtain the energy eigenvalues with the desired accuracy. This procedure simultaneously finds the eigenvalue and its corresponding wave function on a grid, and it was implemented using the UBASIC programming language with a 40 decimal representation for the real variables. This method has been successfully used to study the Hulten potential [34], the confined harmonic oscillator [35] and the spiked oscillator [36]. The second approach, Method II, is based on the discretization of the interval (a, b) according to Numerov's method [32]. To find the energy eigenvalues Lindberg's algorithm is used and the eigenfunctions are obtained by inverse iteration; in this way the convergence of the solution is very fast and increases the efficiency of Numerov's method. This method was used in the study of the confined harmonic oscillator [32].

Regarding the unconfined problem, the energy eigenvalues and eigenfunctions are obtained by moving the boundaries to infinity $(a \to -\infty, b \to +\infty)$. From a practical point of view the energy eigenvalues corresponding to the unconfined case are obtained when the barriers are separated by a large, but finite, distance which is known as practical infinity.

3. Results and discussion

3.1. Unconfined triple-well potentials

We are interested in the study of the anharmonic polynomial potentials with $M = 6$, in Eq. 1, and depending on the coefficients $\{b_n\}$ we can obtain symmetric or asymmetric triple-wells.

The methodologies discussed in the previous section allow us to obtain the energy eigenvalues and eigenfunctions with a high accuracy for the ground state and excited states. In order to see the accuracy of the methods, we start with potentials where the exact eigenvalues are available, namely, $V_1(x) = x^2 - 4x^4 + x^6$ and $V_2(x) = 4x^2 - 6x^4 + x^6$. Chaudhuri and Mondal [19] studied these symmetric triple–well potentials by means of Supersymmetric Quantum Mechanics. For the first one they obtained that the exact ground state energy is -2. Whereas, for the latter they obtained a value of -9, which corresponds to the exact value of the first excited state. Method I provides a ground state energy equal to -2$\pm\epsilon$ for $V_1(x)$, and -9$\pm\epsilon$ for the energy of the first excited state of $V_2(x)$, where the error is $\epsilon \sim 1 \times 10^{-30}$.

Evidently, this method finds the solutions for other States; Some of them are reported in Table I, and they are compared with those obtained by Chaudhuri and Mondal [19]. From the values reported in Table I it is clear that energy eigenvalues obtained with the present method are lower than those obtained by the cited in Ref. 19. In Figs. 1a and 1b the potentials $V_1(x)$ and $V_2(x)$ and their first two lowest states are depicted. It is important to note that $V_2(x)$ has states very close in energy although they are not completely degenerate, as it can be appreciated in Table I. This quasi-degeneracy

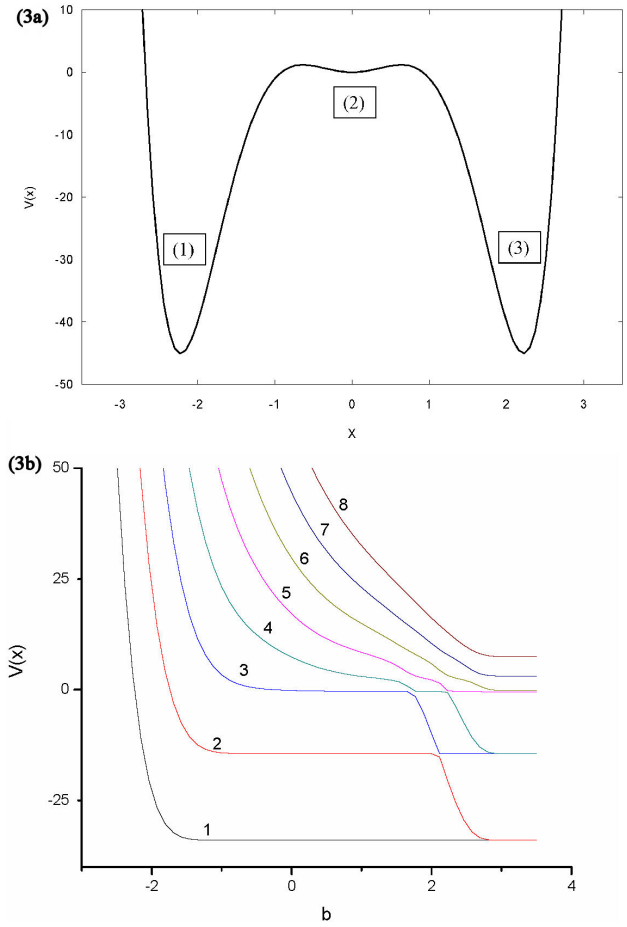

FIGURE 3. In Fig. (3a) we show the triple well potential given by $V(x) = x^6 - 8x^4 + 6x^2$. In Fig. (3b) are plotted the first 8 energy eigenvalues as a function of the position of the right barrier in $x = b$. The left barrier is fixed at $a = -3.5$ units.

is more pronounced in the symmetric triple–well potential: $V_3(x) = 224x^2 - 30x^4 + x^6$. The corresponding eigenvalues of this potential are reported in Table II, rounded to 24 significant figures. These results suggest a clear pattern: these potentials have sets of three almost degenerate states that alternate with an isolated one. It is very important to notice that this conclusion cannot be drawn if one solves the Schrödinger equation with a smaller precision than that used in the present work. In Table II one can see that they are very close but definitively, not degenerate.

The energy eigenvalues corresponding to two symmetric potentials are presented in Table III. Clearly, these potentials have a three-fold quasi-degeneracy, which allows one to conclude that potentials with the form $V(x) = \alpha x^2 - \beta x^4 + x^6$, have a set of three-fold quasi-degenerate states, alternating with an isolated single state, when one of the following conditions is satisfied: $\alpha = (\beta^2/4) \pm 1$, with $\alpha > 0$ and $\beta > 0$. The potential $V(x) = \alpha x^2 - \beta x^4 + x^6$ has three wells if one of the conditions is satisfied [37]: (a) $\beta^2 > 4\alpha$, (b) $\beta^2 = 4\alpha$, or (c) $3\alpha < \beta^2 < 4\alpha$.

On the other hand, the lack of symmetry complicates the use of some methods in the study of asymmetric triple–well

TABLE III. Ground state and the first nine excited state energies for two triple-well potentials that have triplet structure in their spectra.

Potential	Energy
$V(x)=$	
$35x^2-12x^4+x^6$,	$(a=-4.3,\ b=4.3)$
	5.6304919502453345788479019750 1
	5.6379889141049532632855610519 4
	5.6455191498379712435656985854 0
	16.2534395162101494473033311851 5
	24.4896836879793474639282713235 5
	25.2000355605195470607290577697 6
	26.1987957588905725418973530339 5
	32.5555240329271601009600200582 2
	37.1941557815725787012061304400 8
	41.3990543180345566600242851522 5
$V(x)=$	
$99x^2-20x^4+x^6$,	$(a=-4.8, b=4.8)$
	9.7946583898094450854499920393 50
	9.7946583923471354418008817582 44
	9.7946583948848258009043129504 44
	29.0600008702444333623964696657 63
	47.6521762492166828691890061919 28
	47.6521790798012325835672634280 79
	47.6521819103884842674606917675 22
	65.5140139365287067707486459812 44
	82.5704964174012328493437933306 63
	82.5711975252770998798231088283 47
	82.5718987818604622314161594511 05

TABLE IV. Some of the first energy eigenvalues for two asymmetrical triple-well potentials.

Potential	Energy
$V_4(x) =$	
$8x^2+0.3x^3-6x^4+x^6$	$(a=-4.0, b=4.0)$
	0.8027970630719023531385183676 30
	2.2332456131956572807991337871 48
	3.9544638823701811524873914916 95
	7.6192901812387820510004728305 17
	11.6525886361301426924693324105 57
	16.3361921120862016713153633322 88
	21.7927936270423726581286442273 10
	27.9057742438107711210925511534 08
	34.6190911835303478090795605866 96
	41.9004249716572441803267311503 39
	49.7204291793617308737629724323 83
$V_5(x) =$	
$8x^2+0.4x^3-6x^4+x^6$	$(a=-4.0, b=4.0)$
	0.4339138981708549967973246066 88
	2.2475335665342898532249797829 81
	4.1727041939776812448265975464 97
	7.6089033812924343455525064941 96
	11.6317756718103563217521359345 85
	16.3311701783166985947369918620 80
	21.7874193123980163945773716611 35
	27.8989768013208945941504121194 72
	34.6119155890589336795779455489 93
	41.8930507733859217257170010670 541
	49.7129068967829294271411557894 21

potentials. However, with the methods presented in this work it is possible to study the energy spectrum of symmetric and asymmetric triple– well potentials, since symmetry is not a requirement for these algorithms. To illustrate this point, consider the potentials $V_4(x) = 8x^2 + 0.3x^3 - 6x^4 + x^6$ and $V_5(x) = 8x^2 + 0.4x^3 - 6x^4 + x^6$. In Fig. 2 the $V_4(x)$ potential is depicted. The numerical results for the first eleven energy eigenvalues of $V_4(x)$ and $V_5(x)$ are shown in Table IV. From the argumentation concerning the precision of this method, these results can be used as benchmark to validate other methodologies that will be developed in the future to solve similar problems.

3.2. Confined triple–well potentials

In this section two different numerical methods are used to solve the one–dimensional Schrödinger equation with DBC, conditions which are equivalent to those applied for the particle in a box. The main goal is to analyze the dependence of the energy eigenvalues of the 1–D potentials studied here on the size of the box where they are embedded. One needs to solve Eq. (2) subject to the DBC at finite values of x (Eq. 4). It is worth remembering that a and b are the left and right positions of the barrier, respectively. There are other studies where these positions are moved symmetrically, but in the present case the barrier at a is fixed while the barrier at b is displaced to the right, and the Schrödinger equation (2) with DBC is solved to obtain the eigenvalues depending on the size $b-a$ of the box.

Now we are going to consider the triple well potential $V(x) = x^6 - 8x^4 + 6x^2$; two of the wells are symmetrical and identical and very deep respect to the other well located around the origin, as shown in Fig. 3a. In Fig. 3b we show the bahaviour of the first eight energy eigenvalues as a function of the right barrier position $x = b$. The left barrier is fixed at $x = a = -3.5$ units.

When the position of the barrier at the right is b =-1.5, the two states of lower energy are completely inside the well (1); whereas, the other excited states will have energies greater than zero.

TABLE V. The first four energy eigenvalues for the potential $V_4(x)$ confined by a box with walls in a and b.

a	b	E_0	E_1	E_2	E_3
-3.5	-3.0	545.213131	761.592968	981.688153	1255.573099
-3.5	-2.0	43.917489	106.290096	173.600058	245.026089
-3.5	-1.0	2.331169	18.635941	40.300204	66.527630
-3.5	0.0	0.976184	7.009332	15.338126	26.745659
-3.5	1.0	0.828501	3.050105	8.292560	14.136687
-3.5	2.0	0.805833	2.426806	5.242836	8.661214
-3.5	3.0	0.802797	2.233245	3.954463	7.619290
-3.5	3.5	0.802797	2.233245	3.954463	7.619290

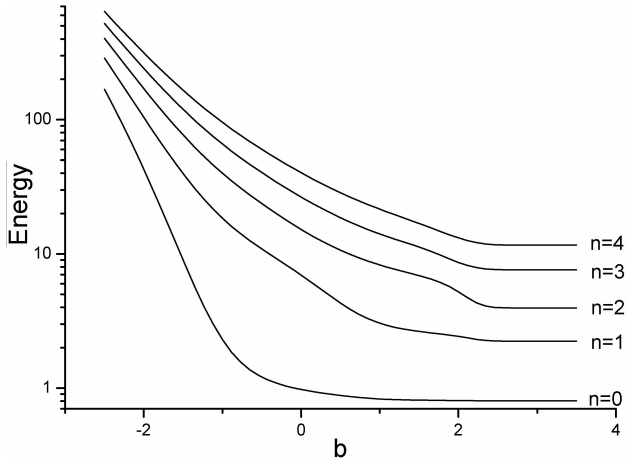

FIGURE 4. The first lowest energy eigenvalues of $V_4(x)$ as a function of the right wall position b for a fixed value of $a = -3$. Note that the energy decreases in a non-monotonic way as b increases.

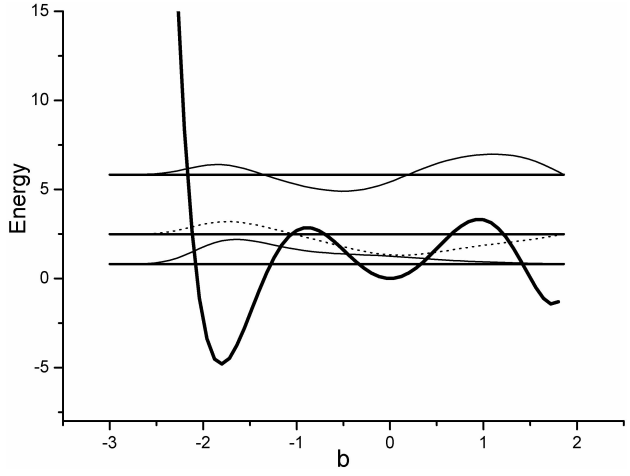

FIGURE 5. First lowest eigenfunctions of the potential $V_4(x)$ for $a = -3$ and $b = 1.9$. The horizontal lines are its eigenvalues for this set on boundary conditions.

As the position of the barrier of the right increases, the square well formed by the two infinite barriers becomes wider, the section of the potential $V(x)$ located inside the well changes its form, and the energy eigenvalues tend to diminish. From Fig. 3b it is observed that the three states of lower energy remain practically constant in the interval form b =-1.5 to b=2.0. This behavior can be understood because in this region the portion of the potential inside the well remains almost without change. Nevertheless, the states of greater energy detect a wider well and have to diminish their values.

For values of b around 2 units, the particle detects the presence of the well (3) and its four lowest energy eigenvalues diminish rapidly, the most excited states detect the third well as a perturbation. Finally, when b is greater than 2.5, the particle detects two deep wells (1) and (3), and the lowest states become quasi degenerated forming pairs of states with its eigenfunction located mainly at the wells (1) and (3).

Now we consider the potential $V_4(x)$ with the confining potential $U(x)$ definied in Eq. (3), fixing the left wall at $a = -3.5$ and changing b from -3.0 to 3.5 in steps of 0.5 units of length. The results are presented in Table V, and a plot of the energy eigenvalues as a function of b is depicted in Fig. 4, where the drastic change in the energy is evident when b increases. From this figure one can notice that E_2 departs from E_3 and approaches E_1 at $b = 2$. In Fig. 5 the three lowest states corresponding to the $V_4(x)$ potential for $a = -3$ and $b = 1.9$ are shown.

In previous works the walls were moved symmetrically with respect to the origin and it was found that the energy eigenvalues decrease monotonically. However, when the displacement of the barriers is asynchronous, the monotonic behavior is lost and one can only say that the eigenvalues decrease as a function of the size of the wall.

4. Conclusions

One–dimensional triple–well potentials are studied by two different numerical approaches. These two methods are very useful to study free (unbounded) and bounded quantum problems. It is found that these triple–well potentials have singlet, doublet and triplet states. The energies provided by the present approach are lower in energy than those previously reported. An empirical formula that predicts the existence of three–fold degenerate states is presented.

The major utility of the methods presented in this work is to study confined quantum problems particularly when the boundaries are non-symmetrically imposed, in which case the solution by other techniques becomes very difficult. When the walls are displaced symmetrically with respect to the origin, the energy decreases monotonically as a function of the positions of the walls. Fixing the position of the left wall and moving the other wall to the right, breaks this monotonicity. The multiplicity of states varies with the positions of the walls in a way that is difficult to predict, except when the walls are far from the origin, where one recovers the spectrum of the free (unconfined) problem.

The methods of this work are accurate, efficient and allow the possibility to study one–dimensional quantum problems with polynomial and non-polynomial potentials with very general boundary conditions.

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