Excited-state energy eigenvalue and wave-function evaluation of the Gaussian symmetric double-well potential problem via numerical shooting method 1

Sutee Boonchui · Artit Hutem

Abstract   This work aims at computing excited-state energy eigenvalues and wave-function of a particle under Gaussian symmetric double-wells potential using numerical shooting method and perturbation theory a method to deal with discrete-eigenvalue problems. We also compare the energy eigenvalue and wave-function with those obtained from other typical means popular among physics students, namely the numerical shooting method and perturbation theory. Show that the idea of program of the numerical shooting method and perturbation theory of this problem (see Sects. 2.2 and 3). The numerical shooting method is generally regarded as one of the most efficient methods that give very accurate results because it integrates the Schrödinger equation directly, though in the numerical sense. The $n =$ even case is shown in Fig. 5. In this case, the wave-function has split up on symmetric nodes under Gaussian symmetric double-well potential.

1 Introduction

In quantum mechanics, the stationary-state Schrödinger equation for complex systems is generally too difficult to solve exactly and one must again rely on approximation methods. There exist several means to study them, e.g. time-independent perturbation

S. Boonchui (✉) · A. Hutem
Forum for Theoretical and Computational Physics, Department of Physics, Faculty of Science,
Kasetsart University, Bangkok 10900, Thailand
e-mail: fscistb@ku.ac.th

A. Hutem
e-mail: magoohootem@yahoo.com

theory [1], the WKB approximation [2], the variation method [1–3] and the analytical transfer matrix method [4,5] etc. The Schrödinger equation have proposed various analytical and numerical methods for the solution of this central quantum mechanics equation, approaches even to one-dimensional solutions are still a subject of debate. This is confirmed by the continuing appearance of new publications in this field [6–8]. Boyd L. Earl used the harmonic oscillator Gaussian perturbation to evaluate frequency "doubling" in the vibrational spectrum of ammonia [9]. In this project we present two of the most important types of approximation methods which are useful under different conditions.

The scheme of the paper is as follows. In Sect. 2.1 detailing with the perturbation theory and calculation of energy eigenvalue for Gaussian symmetric double-well potential. In Sect. 2.3 the Schrödinger equation and the potential in terms of the new variable and parameter is given by

$$\frac{d^2\psi(\xi)}{d\xi^2} + \left(\varepsilon - \xi^2 - 2ae^{-b\xi^2}\right)\psi(\xi) = 0, \quad V(\xi) = \xi^2 + 2ae^{-b\xi^2}.$$

The numerical shooting method and result is given in Sect. 3. The main principle of numerical shooting method is to subdivide the domain into many tiny segment each of which possesses a constant potential. We conclude with a Discussion section.

2 Basic theory

2.1 Time-independent perturbation theory: the non-degenerate

The approximation method we consider here is time-independent perturbation theory [1–3] sometimes known as the Rayleigh–Schrödinger perturbation theory. Consider a system whose Hamiltonian can be dissociated into separate parts, one part corresponding to the unperturbed system and the other part representing the perturbation. We can write the total Hamiltonian then as

$$\hat{H} = \hat{H}_{(0)} + gV \tag{1}$$

where $\hat{H}_{(0)}$ represents the unperturbed part of the Hamiltonian whose eigenfunction and eigenvalues are assumed to be known and V is a small perturbative potential of the order of g in smallness. Suppose the problem to be solved is of the Schrödinger form

$$\hat{H}\psi_n = E_n\psi_n, \tag{2}$$

assuming that the unperturbed problem

$$\hat{H}_{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \tag{3}$$

has already been solved. In the example mentioned above, that of a hydrogen atom in an external electric field, $\hat{H}_{(0)}$ is the Hamiltonian describing the unperturbed hydrogen

atom with eigenfunctions $\psi_n^{(0)}$ and gV is the perturbation corresponding to the applied field.

From our supposition that the perturbation is small, it is reasonable to assume that the energy eigenvalues for the complete problem can be written as

$$E_n = E_n^{(0)} + gE_n^{(1)} + g^2 E_n^{(2)} + \cdots \tag{4}$$

where $E_n^{(0)}$ is the unperturbed energy eigenvalue and $gE_n^{(1)}$ is the first-order correction to the energy, $g^2 E_n^{(2)}$ is the second-order correction to the energy, etc. The wave-function can also be expand in powers of the perturbation parameter g as

$$\psi_n = \psi_n^{(0)} + g\psi_n^{(1)} + g^2 \psi_n^{(2)} + \cdots . \tag{5}$$

By substituting Eqs. (1), (4) and (5) into Eq. (2), we obtain

$$\begin{aligned}
&\left(\hat{H}_{(0)} + gV\right)\left(\psi_n^{(0)} + g\psi_n^{(1)} + g^2 \psi_n^{(2)} + \cdots\right) \\
&= \left(E_n^{(0)} + gE_n^{(1)} + g^2 E_n^{(2)} + \cdots\right)\left(\psi_n^{(0)} + g\psi_n^{(1)} + g^2 \psi_n^{(2)} + \cdots\right).
\end{aligned} \tag{6}$$

Expanding out both sides of the above yields

$$\begin{aligned}
\hat{H}_{(0)}\psi_n^{(0)} &+ g\hat{H}_{(0)}\psi_n^{(1)} + g^2\hat{H}_{(0)}\psi_n^{(2)} + \cdots + gV\psi_n^{(0)} + g^2 V\psi_n^{(1)} + g^3 V\psi_n^{(2)} + \cdots \\
&= E_n^{(0)}\psi_n^{(0)} + gE_n^{(0)}\psi_n^{(1)} + \cdots + gE_n^{(1)}\psi_n^{(0)} + g^2 E_n^{(1)}\psi_n^{(1)} + g^3 E_n^{(1)}\psi_n^{(2)} + \cdots \\
&\quad + g^2 E_n^{(2)}\psi_n^{(0)} + g^3 E_n^{(2)}\psi_n^{(1)} + g^4 E_n^{(2)}\psi_n^{(2)} + \cdots .
\end{aligned} \tag{7}$$

The factor g reflects the order of approximation in the expansion of the eigenvalue eigenvectors, and the potential. Zeroth order corresponds to $g = 0$, the unperturbed solution. First order corresponds to g, second order to g^2, etc. In order for the equality to hold, terms of the same order must be equal. Therefore, equating terms of equal order, which are easily grouped since the power of g in each term determines its order, yields

$$\hat{H}_{(0)}\psi_n^{(0)} = E_n^{(0)}\psi_n^{(0)} \tag{8}$$

for zeroth order,

$$\hat{H}_{(0)}g\psi_n^{(1)} + gV\psi_n^{(0)} = E_n^{(0)}g\psi_n^{(1)} + gE_n^1\psi_n^{(0)} \tag{9}$$

for first order, and

$$g^2\hat{H}_{(0)}\psi_n^{(2)} + g^2 V\psi_n^{(1)} = g^2 E_n^{(0)}\psi_n^{(2)} + g^2 E_n^{(1)}\psi_n^{(1)} + g^2 E_n^{(2)}\psi_n^{(0)} \tag{10}$$

for second order.

The first-order term leads to an expression for the first-order correction to the energy eigenvalues. This can be determined as follows. Dividing out the factor of g from Eq. (9) yields

$$\hat{H}_{(0)}\psi_n^{(1)} + V\psi_n^{(0)} = E_n^{(0)}\psi_n^{(1)} + E_n^1\psi_n^{(0)}. \tag{11}$$

Multiplying through on each side by the complex conjugate of $\psi_n^{(0)}$ and integrating over all space, we find that Eq. (11) becomes

$$\int \psi_n^{(0)*}\hat{H}_{(0)}\psi_n^{(1)}d^3r + \int \psi_n^{(0)*}V\psi_n^{(0)}d^3r = \int \psi_n^{(0)*}E_n^{(0)}\psi_n^{(1)}d^3r + \int \psi_n^{(0)*}E_n^1\psi_n^{(0)}d^3r. \tag{12}$$

Making use of the hermiticity of $\hat{H}_{(0)}$ we can write the first term on the left-hand side of Eq. (12) as

$$\int \psi_n^{(0)*}\hat{H}_{(0)}\psi_n^{(1)}d^3r = \int \left(\hat{H}_{(0)}\psi_n^{(0)}\right)^*\psi_n^{(1)}d^3r = \int \psi_n^{(0)*}E_n^{(0)}\psi_n^{(1)}d^3r. \tag{13}$$

Therefore the expression for $E_n^{(1)}$, the first-order correction to the energy, is

$$E_n^{(1)} = \frac{\int \psi_n^{(0)*}V(r)\psi_n^{(0)}d^3r}{\int \psi_n^{(0)*}\psi_n^{(0)}d^3r}. \tag{14}$$

To find the second-order correction to the energy, we start with the second-order equation, Eq. (10):

$$\hat{H}_{(0)}\psi_n^{(2)} + V\psi_n^{(1)} = E_n^{(0)}\psi_n^{(2)} + E_n^{(1)}\psi_n^{(1)} + E_n^{(2)}\psi_n^{(0)}. \tag{15}$$

Multiply Eq. (15) on each side by $\psi_n^{(0)*}$ and integrate over all space to yield

$$\int \psi_n^{(0)*}V\psi_n^{(1)}d^3r = E_n^{(1)}\int \psi_n^{(0)*}\psi_n^{(1)}d^3r + E_n^{(2)}\int \psi_n^{(0)*}\psi_n^{(0)}d^3r. \tag{16}$$

By substituting

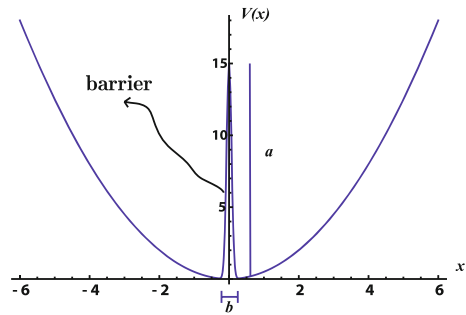$$\psi_n^{(1)} = \sum_m A_m\psi_m^{(0)},$$

$$\psi_{n'}^{(1)} = -\sum_{m\neq n'}\frac{V_{mn'}}{\left[E_m^{(0)} - E_{n'}^{(0)}\right]}\psi_m^{(0)}$$

back into the right-hand side and left-hand side, respectively of Eq. (16), we get

$$E_n^{(2)} = \sum_{m\neq n}\frac{|V_{mn}|^2}{E_n^{(0)} - E_m^{(0)}}, \tag{17}$$

where $V_{mn} = \langle m|V|n\rangle = \int \psi_m^{(0)*}V\psi_n^{(0)}d^3r$.

Fig. 1 Potential energy of the Gaussian symmetric double-well. By setting $a = 15, \; b = 100$

2.2 The perturbation theory: Gaussian symmetric double-well potential

Suppose a particle is bound to a center of attraction by the Gaussian harmonic oscillator symmetric double-well potential [9] (see Fig. 1)

$$V(x) = \frac{1}{2}m\omega^2 x^2 + ae^{-bx^2} \tag{18}$$

where a and b are relatively small. If a and b were zero, this would be the potential energy of a harmonic oscillator. Therefore, for small values of a, b and ae^{-bx^2} may be treated as a perturbation to the potential $\frac{1}{2}m\omega^2 x^2$. In this case, the well-known harmonic oscillator solutions for $\psi_n^{(0)}$ and $E_n^{(0)}$ are

$$\psi_n^{(0)}(\xi) = A_n H_n(\xi)e^{-\xi^2/2},$$
$$E_n^{(0)} = \left(n + \frac{1}{2}\right)\hbar\omega, \; n = 0, 1, 2, 3, \ldots \tag{19}$$

where $A_n = \left(2^n n!\right)\left(\frac{m\omega}{\pi\hbar}\right)^{\frac{1}{4}}$ is the normalized factor. The polynomials $H_n(\xi)$ are, except for the normalization constants, the Hermite polynomial $H_n(\xi)$, whose properties can be found in any number of textbooks on mathematical physics. By substituting Eqs. (19), (18) and using the Hermite polynomial properties into Eq. (14), we can now finally write the total energy eigenvalue for Gaussian symmetric double-well potential. They are

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega + \int_{-\infty}^{\infty} \left(\psi_n^{(0)}(\xi)\right)^2 \left(ae^{-bx^2}\right)dx. \tag{20}$$

Logic of calculate energy eigenvalues by the perturbation theory of Gaussian symmetric double-well potential

– Input values a, b, n in mathematica programm.
– Input the wave-function to the harmonic oscillator in mathematica programm.
– Calculate energy eigenvalue.

For example, numerical evaluation of energy of Gaussian symmetric double-well potential. Consider the following program:

– In[1]:= Clear[a,b,n]
– In[2]:= $a = 5$; $b = 100$; $n = 2$;
– In[3]:= $\psi[n\_, \ x\_] := \frac{HermiteH[n, \ x]Exp[-\frac{x^2}{2}]}{\sqrt{2^n n! \sqrt{\pi}}}$;
– In[4]:= $SetPrecision[N[\left(\int_{-\infty}^{\infty}(a \ Exp[-bx^2])Abs[\psi[n, x]]^2 \ dx\right) + (2n+1)]$, 15]
– Out[4]:= 5.24390652819528

2.3 Gaussian symmetric double-well potential

We shall start with the time-independent Schrödinger in one dimension

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x). \tag{21}$$

Substituting Eq. (18) into Eq. (21) and multiplying by $\frac{2m}{\hbar^2}$, we have

$$\frac{d^2\psi(x)}{dx^2} + \left(\frac{2mE}{\hbar^2} - \frac{m^2\omega^2 x^2}{\hbar^2} - \frac{2ma}{\hbar^2}e^{-bx^2}\right)\psi(x) = 0. \tag{22}$$

After introducing new variable and parameter as $x = \alpha\xi$, $\varepsilon = \frac{2E}{\hbar\omega}$, $m, \hbar, \omega = 1, \alpha^4 = \frac{\hbar^2}{m^2\omega^2}$, the Schrödinger equation is then transformed to

$$\frac{d^2\psi(\xi)}{d\xi^2} + \left(\varepsilon - \xi^2 - 2ae^{-b\xi^2}\right)\psi(\xi) = 0. \tag{23}$$

Also, the potential in terms of the new variable and parameter is given by

$$V(\xi) = \xi^2 + 2ae^{-b\xi^2}. \tag{24}$$

We can find the numerical solution to Eq. (23) by dividing ξ into many small segments, each of $\triangle\xi$ in length. The second derivative in Eq. (23) can be approximated in finite difference [10–13] form as follows,

$$\frac{d^2\psi(\xi)}{d\xi^2} \approx \frac{\psi_{i+1} + \psi_{i-1} - 2\psi_i}{\left(\triangle\xi\right)^2}. \tag{25}$$

By substituting Eq. (25) back into Eq. (23), we obtain

$$\psi_{i+1} = 2\psi_i - \psi_{i-1} - \left(\triangle\xi\right)^2\left(\varepsilon - \xi^2 - 2ae^{-b\xi^2}\right)\psi_i \ ; \ i = 2, 3, 4, \ldots, \tag{26}$$

where $\xi_{i+1} = \triangle\xi + \xi_i$ or $\xi_i = \triangle\xi + \xi_{i-1}$. The special potential given by Gaussian symmetric double-well potential has been used in evaluate Eq. (26) in mathematica program (see Sect. 3).

3 Numerical shooting method and result

We define the new variables for using in evaluating the excited-state energy eigenvalues and wave-function of the Gaussian symmetric and asymmetric double-wells potential.

1. ξ_{min} is the begin position in the study range.
2. ξ_{max} is the ultimate position in the study range.
3. ξ is any position in the study range.
4. nn is a number of tiny bars in the study range.
5. $\triangle\xi$ is the length of tiny bars so that

$$\triangle\xi = \frac{\xi_{max} - \xi_{min}}{nn}. \tag{27}$$

3.1 Logic of the numerical shooting method [11,14] calculation of energy for the Gaussian symmetric double-well potential

– Input values ξ_{min} and ξ_{max} in mathematica program.
– Input the period amount.
– Input Eq. (26) into mathematica program.

Find the initial value for calculation. Input the initial condition by setting $\psi_1 = 0$ for the position imprisons and set $\frac{d\psi}{d\xi} = 1$ from the slope of position 1 and 2, so that

$$\frac{d\psi}{d\xi} \approx \frac{\psi_2 - \psi_1}{\triangle\xi} \Rightarrow \psi_2 \approx \triangle\xi. \tag{28}$$

By input ψ_1 and ψ_2 as two initial values for calculation, we can find ψ_3 from Eq. (26). In the same way, we can find ψ_4 by substituting ψ_2 and ψ_3 in the equation. Keep doing this, we can find ψ_n (see Fig. 2).

– The next task is to calculate wave-function in Eq. (26) (ψ_{i+1}) so that it approaches zero as closely as desired. Normally, we assign a small value as the standard to make sure wave-function in Eq. (26) get close enough to zero. For example, if $|\psi_{i+1}| \leq 10^{-6}$, we stop the calculation and accept the final energy as the numerical solution (see also the flowchart Fig. 3 and see Tables 1, 2, 3, 4 and 5).
– Plot wave-function by the graph related to i.

For example, numerical evaluation of energy eigenvalue of the numerical shooting method for the Gaussian symmetric double-well potential. Consider one way to write the program [15,16]:

Fig. 2 Interpolation of wave-function
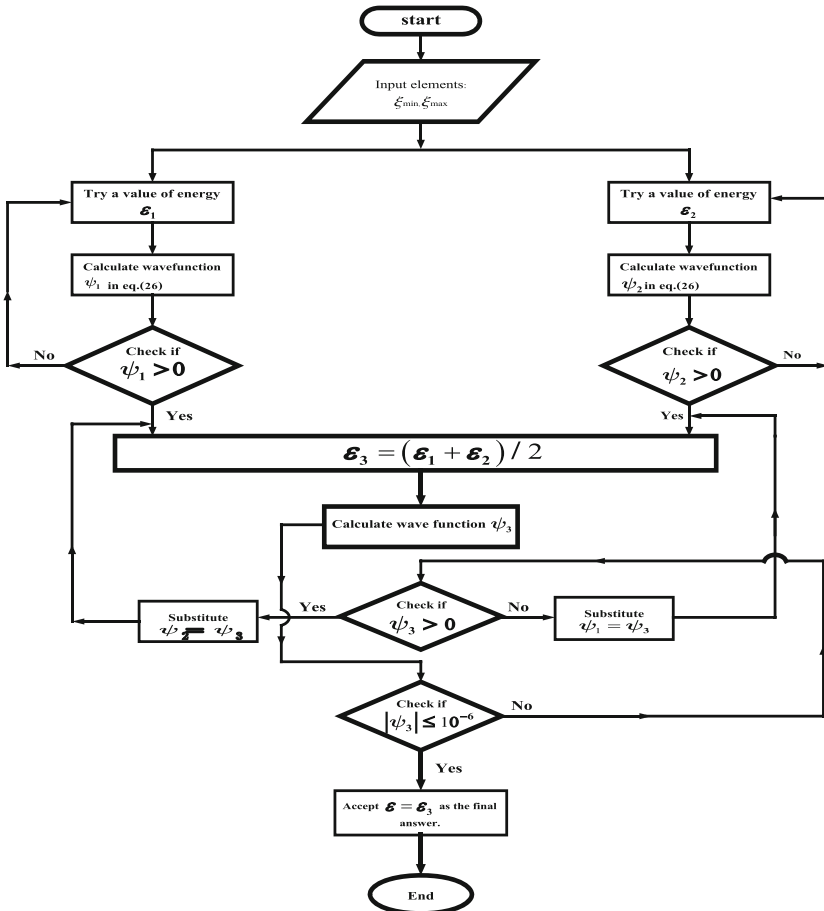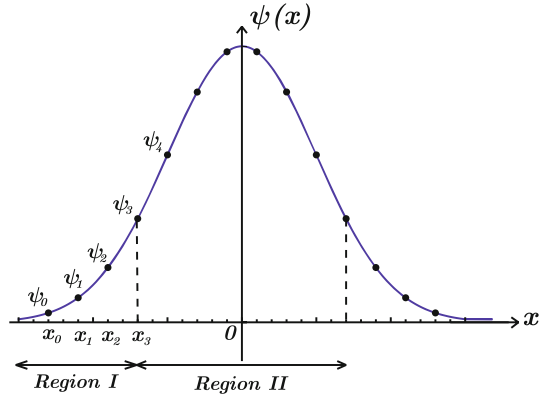
Fig. 3 The flowchart schematic energy eigenvalue and wave-function evaluation procedures

Table 1 Comparison of **energy spectrum** of the potential $V(x) = \frac{1}{2}m\omega^2 x^2 + ae^{-bx^2}$ (the Gaussian symmetric double-well potential) obtained from numerical shooting method (NSM), perturbation theory (PT)

b	State	Energy via NSM	Energy via PT	Difference (%)
100	$n = 0$	1.752692547716	1.497518595105	15.701990
	$n = 1$	3.006406272834	3.004925926684	0.049250
	$n = 2$	5.467572940039	5.243906528196	4.176200
	$n = 3$	6.998440556415	7.00724382589	0.125710
	$n = 4$	9.340942317245	9.179433033049	1.744130
250	$n = 0$	1.533384315164	1.315597201549	15.288770
	$n = 1$	2.998702324086	3.001257359369	0.085170
	$n = 2$	5.307882284000	5.156548755505	2.892340
	$n = 3$	6.987067192979	7.001871060749	0.211650
	$n = 4$	9.216789512336	9.116489061541	1.094190
500	$n = 0$	1.472432142490	1.223383525804	18.476680
	$n = 1$	2.997022523504	3.000445875301	0.114160
	$n = 2$	5.267365393462	5.111247222557	3.008460
	$n = 3$	6.984568085335	7.000666147481	0.230210
	$n = 4$	9.185903841257	9.083104668263	1.125390
750	$n = 0$	1.467299537059	1.182452591292	21.499890
	$n = 1$	2.997883892392	3.000242946193	0.112060
	$n = 2$	5.264029226103	5.090983834698	3.342250
	$n = 3$	6.984361833334	7.000363449876	0.228840
	$n = 4$	9.183373801410	9.068056997575	1.263650
1,000	$n = 0$	1.466877319880	1.158034885310	23.531360
	$n = 1$	2.996872505631	3.000157877008	0.109570
	$n = 2$	5.263755301689	5.078859802226	3.575410
	$n = 3$	6.984344892503	7.000236342748	0.227270
	$n = 4$	9.183166152239	9.059027093324	1.361010

Setting $a = 5$, $n = 100$ at range $5(\xi_{max} = 5)$, $\xi_{min} = -5$. All energies are in the $\hbar\omega/2$ unit

- In[1] := $\xi_{min} = -5$
- Out[1] = -5

- In[2] := $\xi_{max} = 5$
- Out[2] = 5

- In[3] := nn = 100
- Out[3] = 100

- In[4] := $\triangle\xi = N\left(\frac{\xi_{max} - \xi_{min}}{nn}\right)$
- Out[4] = 0.1

Table 2 Comparison of **energy spectrum** of the potential $V(x) = \frac{1}{2}m\omega^2 x^2 + ae^{-bx^2}$ (the Gaussian symmetric double-well potential) obtained from numerical shooting method (NSM), perturbation theory (PT))

b	State	Energy via NSM	Energy via PT	Difference (%)
2,500	$n = 0$	1.466839556202	1.099980005998	28.584760
	$n = 1$	2.996871487316	3.000039976012	0.105670
	$n = 2$	5.263730805324	5.049950050963	4.145570
	$n = 3$	6.984343377479	7.000059916082	0.224770
	$n = 4$	9.183147585392	9.037432622099	1.599450
5,000	$n = 0$	1.466839556188	1.070703608111	31.222010
	$n = 1$	2.996871487311	3.000014137894	0.104810
	$n = 2$	5.263730805320	5.035337670402	4.435220
	$n = 3$	6.984343377476	7.000021198361	0.224220
	$n = 4$	9.183147585389	9.026492661038	1.720570

Setting $a = 5, n = 100$ at range $5(\xi_{max} = 5), \xi_{min} = -5$. All energies are in the $\hbar\omega/2$ unit

- In[5] := $\psi_1 = 0$
- Out[5] = 0

- In[6] := $N[\psi_2 = \triangle\xi]$
- Out[6] = 0.1

- In[7] := $\xi_1 = -5$
- Out[7] = -5

- In[8] := $\xi_2 = \xi_1 + \triangle\xi$
- Out[8] = -4.9

- In[9] := $a = 15$
- Out[9] = 15

- In[10] := $b = 100$
- Out[10] = 100

- In[11] := $\varepsilon = 6.149308307701721251099$
- Out[11] = 6.149308307701721251099
- In[12] := $N[Table[\psi_{i+1} = 2\psi_i - \psi_{i-1} - (\triangle\xi)^2(\varepsilon - (\xi_{i+1} = \xi_i + \triangle\xi)^2 - 2ae^{-b(\xi_{i+1} = \xi_i + \triangle\xi)^2})\psi_i, \{i, 2, 99\}]]$

- Out[12] = {0.216891, 0.368355, 0.575113, 0.862965, 1.26482, 1.82276, 2.59015, 3.63367, 5.03514, 6.89282, 9.32196, 12.454, 16.4343, 21.4172, 27.5589, 35.0071, 43.8874, 54.2864, 66.233, 79.6769, 94.4679, -171.814, -169.667, -157.247, -136.083, -121.584, -136.083, -157.247, -169.668, -171.814, -163.67, -145.87, -119.626, -86.6116, -48.8256, -8.43257, 32.3947,

Table 3 Comparison of **energy spectrum** of the potential $V(x) = \frac{1}{2}m\omega^2 x^2 + ae^{-bx^2}$ (the Gaussian symmetric double-well potential) obtained from numerical shooting method (NSM), perturbation theory (PT))

b	State	Energy via NSM	Energy via PT	Difference (%)
100	$n = 0$	2.418185720097	2.492555785315	3.028870
	$n = 1$	3.023665134298	3.014777780053	0.294360
	$n = 2$	6.149308307702	5.731719584586	7.029510
	$n = 3$	7.023989189229	7.021731347766	0.032150
	$n = 4$	9.968815889955	9.538299099154	4.413950
250	$n = 0$	2.118540714508	1.946791604646	8.449450
	$n = 1$	3.002280199644	3.003772078106	0.049680
	$n = 2$	5.812101015495	5.469646266516	6.070950
	$n = 3$	6.992391233519	7.005613182245	0.188910
	$n = 4$	9.646771994233	9.349467184625	3.130140
500	$n = 0$	2.017526037898	1.670150577413	18.839810
	$n = 1$	2.997324016352	3.001337625903	0.133820
	$n = 2$	5.712722979579	5.333741667672	6.861590
	$n = 3$	6.985016646422	7.001998442442	0.242820
	$n = 4$	9.559026424884	9.249314004791	3.293350
750	$n = 0$	2.008585914002	1.547357773877	25.941250
	$n = 1$	2.996908698645	3.000728838580	0.127390
	$n = 2$	5.704267026740	5.272951504094	7.858380
	$n = 3$	6.984398739338	7.001090349629	0.238690
	$n = 4$	9.551706206798	9.204170992725	3.705880
1,000	$n = 0$	2.007847384138	1.474104655931	30.657670
	$n = 1$	2.996874542244	3.000473631025	0.120020
	$n = 2$	5.703570906073	5.236579406677	8.537200
	$n = 3$	6.984347922564	7.000709028245	0.233980
	$n = 4$	9.551104572415	9.177081279974	3.994230

Setting $a = 15$, $n = 100$ at range $5(\xi_{max} = 5)$, $\xi_{min} = -5$. All energies are in the $\hbar\omega/2$ unit

    71.6218, 107.476, 138.538, 163.795, 182.666, 194.981, 200.94, 201.054, 196.062, 186.856, 174.4, 159.661, 143.549, 126.879, 110.337, 94.4683, 79.6773, 66.2334, 54.2868, 43.8878, 35.0077, 27.5595, 21.4179, 16.4352, 12.4551, 9.32328, 6.8945, 5.03733, 3.63658, 2.59405, 1.82807, 1.27214, 0.873205, 0.589626, 0.389188, 0.24717, 0.144553, 0.066352, $1.74818 * 10^{-6}$}

- In[13]:= SetPrecision[1/2 (6.149308307748287379825946445242743542
  $\qquad$ +6.149308307655155122372530110401867), 15]
- Out[13]= 6.149308307701721251099

- In[14] := {0, 0.1, 0.2168906916922983', 0.36835525985655915', 0.57511250041 02523', 0.8629645815306629', 1.2648202529308215', 1.82276349220692', 2.59 0154864652286', 3.6336746615712987', 5.035136546502864', 6.892816630199 291', 9.321958889621007', 12.454041328591837', 16.43433012568447', 21.417

Table 4 Comparison of **energy spectrum** of the potential $V(x) = \frac{1}{2}m\omega^2 x^2 + ae^{-bx^2}$ (the Gaussian symmetric double-well potential) obtained from numerical shooting method (NSM), perturbation theory (PT)

b	State	Energy via NSM	Energy via PT	Difference (%)
2,500	$n = 0$	2.007781306004	1.299940017994	42.799330
	$n = 1$	2.996871487311	3.000119928036	0.108310
	$n = 2$	5.703508640296	5.149850152889	10.202530
	$n = 3$	6.984343377501	7.000179748246	0.226480
	$n = 4$	9.551050765812	9.112297866298	4.701760
5,000	$n = 0$	2.007781305984	1.212110824334	49.422180
	$n = 1$	2.996871487310	3.000042413682	0.105750
	$n = 2$	5.703508640225	5.106013011206	11.054990
	$n = 3$	6.984343377501	7.000063595084	0.224820
	$n = 4$	9.551050765514	9.079477983115	5.062370

Setting $a = 15, n = 100$ at range $5(\xi_{max} = 5), \xi_{min} = -5$. All energies are in the $\hbar\omega/2$ unit

Table 5 The energy eigenvalues of the gaussian symmetric double-well potential ($V(x) = \frac{1}{2}m\omega^2 x^2 + ae^{-bx^2}$) from numerical shooting method and perturbation theory (PT) energy eigenvalues by setting $b = 250$ and $N = 100$ at range $5(\xi_{max} = 5), \xi_{min} = -5$

a	State	Energy via NSM	Energy via PT	Difference (%)
1.0	$n = 2$	5.057074285171	5.031309751101	0.510780
1.5	$n = 2$	5.089419530402	5.046964626652	0.837670
2.0	$n = 2$	5.121542697074	5.062619502202	1.157150
2.5	$n = 2$	5.153410129179	5.078274377753	1.468690
3.0	$n = 2$	5.184990223823	5.093929253303	1.771800
3.5	$n = 2$	5.216253540525	5.109584128854	2.066070
4.0	$n = 2$	5.247172879148	5.125239004404	2.351120
4.5	$n = 2$	5.277723327978	5.140893879955	2.626630
5.0	$n = 2$	5.307882284000	5.156548755506	2.892340
5.5	$n = 2$	5.337629447586	5.172203631056	3.148020
6.0	$n = 2$	5.366946794326	5.187858506607	3.393490
6.5	$n = 2$	5.395818526740	5.203513382157	3.628630
7.0	$n = 2$	5.424231008603	5.219168257708	3.853330
7.5	$n = 2$	5.452172684995	5.234823133258	4.067550
12.5	$n = 2$	5.704437503242	5.391371888764	5.642950

All energies are in the $\hbar\omega/2$ unit

226735439613', 27.558943452889878', 35.00714471309648', 43.887380333792
564', 54.28642287966756', 66.23300397261916', 79.67690908393936', 94.4679
050778218', 110.33648861681517', 126.87888792536509', 143.54904373333
63', 159.66035118842728', 174.39968398165038', 186.8555872238962', 196.06
1495714152', 201.05343818881926', −169.66735721544626', −157.246636255
143', −136.08325526435792', −121.58397324756969', −136.083309837305

Fig. 4 The wave-function of Gaussian symmetric double-well potential in case of second excited-state energy via numerical shooting method (ε_2), $a = 15$, $b = 100$ at range $5(\xi_{max} = 5)$
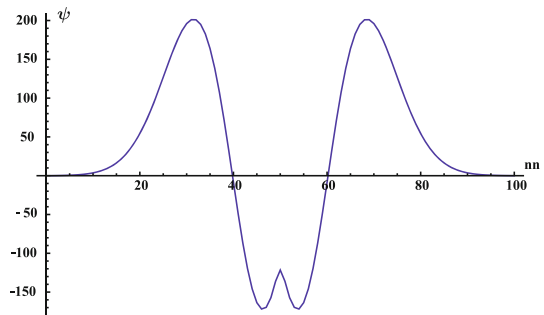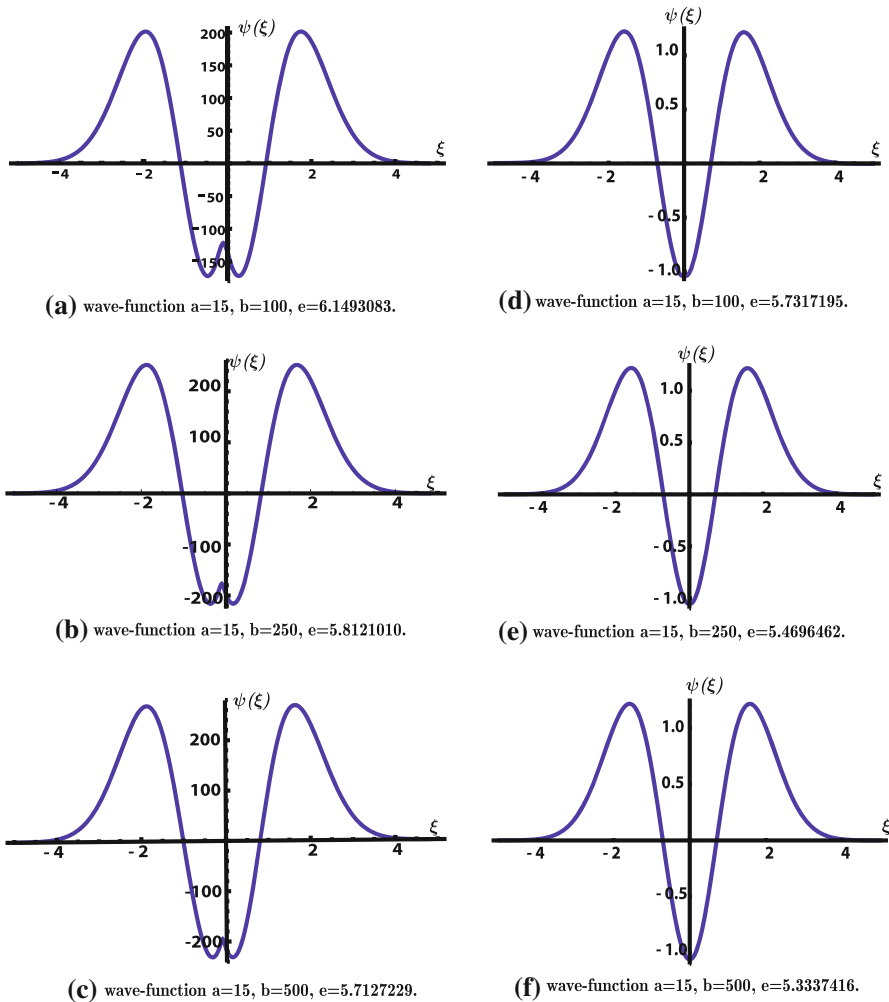

73', −157.24674807351738', −169.66752006232556', −171.81389550314898', −163.66981282734838', −145.87034328690606', −119.62598984408189', −86.61163281984116', −48.825573913220815', −8.432567082368823', 32.394 658625808106', 71.62181226922888', 107.47607395732834', 138.537646150 657', 163.79544922450177', 182.6663627390982', 194.98081732052358', 200.9 4024592459644', 201.05370326046872', 196.06178720650595', 186.855898871 88527', 174.40001036475516', 159.66068803328665', 143.54938814541438', 126.87923856383703', 110.33684583474478', 94.46827105670927', 79.6772 8799847546', 66.23340222908045', 54.28684948140477', 43.88784744190597', 35.00766849275775', 27.5595453303101', 21.41793524377164', 16.4351836001 2976', 12.455091836994969', 9.323277978870514', 6.894503768748625', 5.037 33160980757', 3.636576537549865', 2.5940494081606533', 1.82806588852133 74', 1.2721397840640816', 0.873204528253243', 0.589625630513128', 0.38918 80250704389', 0.24717023417441794', 0.14455308826327257', 0.06635195882 237235', 1.7481785367576275' ∗⁻ 6}

– Out[14]= {0, 0.1, 0.216891, 0.368355, 0.575113, 0.862965, 1.26482, 1.82276, 2.59015, 3.63367, 5.03514, 6.89282, 9.32196, 12.454, 16.4343, 21.4172, 27.5589, 35.0071, 43.8874, 54.2864, 66.233, 79.6769, 94.4679, 110.336, 126.879, 143.549, 159.66, 174.4, 186.856, 196.061, 201.053, 200.94, 194.981, 182.666, 163.795, 138.538, 107.476, 71.6219, 32.3948, −8.4324, −48.8254, −86.6114, −119.626, −145.87, −163.67, −171.814, −169.667, −157.247, −136.083, −121.584, −136.083, −157.247, −169.668, −171.814, −163.67, −145.87, −119.626, −86.6116, −48.8256, −8.43257, 32.3947, 71.6218, 107.476, 138.538, 163.795, 182.666, 194.981, 200.94, 201.054, 196.062, 186.856, 174.4, 159.661, 143.549, 126.879, 110.337, 94.4683, 79.6773, 66.2334, 54.2868, 43.8878, 35.0077, 27.5595, 21.4179, 16.4352, 12.4551, 9.32328, 6.8945, 5.03733, 3.63658, 2.59405, 1.82807, 1.27214, 0.873205, 0.589626, 0.389188, 0.24717, 0.144553, 0.066352, $1.74818 * 10^{-6}$}

– In[15] := $ListPlot[\%, PlotJoined \rightarrow True]$
– Out[15] = graph see Fig. 4

(a) wave-function a=15, b=100, e=6.1493083.

(d) wave-function a=15, b=100, e=5.7317195.

(b) wave-function a=15, b=250, e=5.8121010.

(e) wave-function a=15, b=250, e=5.4696462.

(c) wave-function a=15, b=500, e=5.7127229.

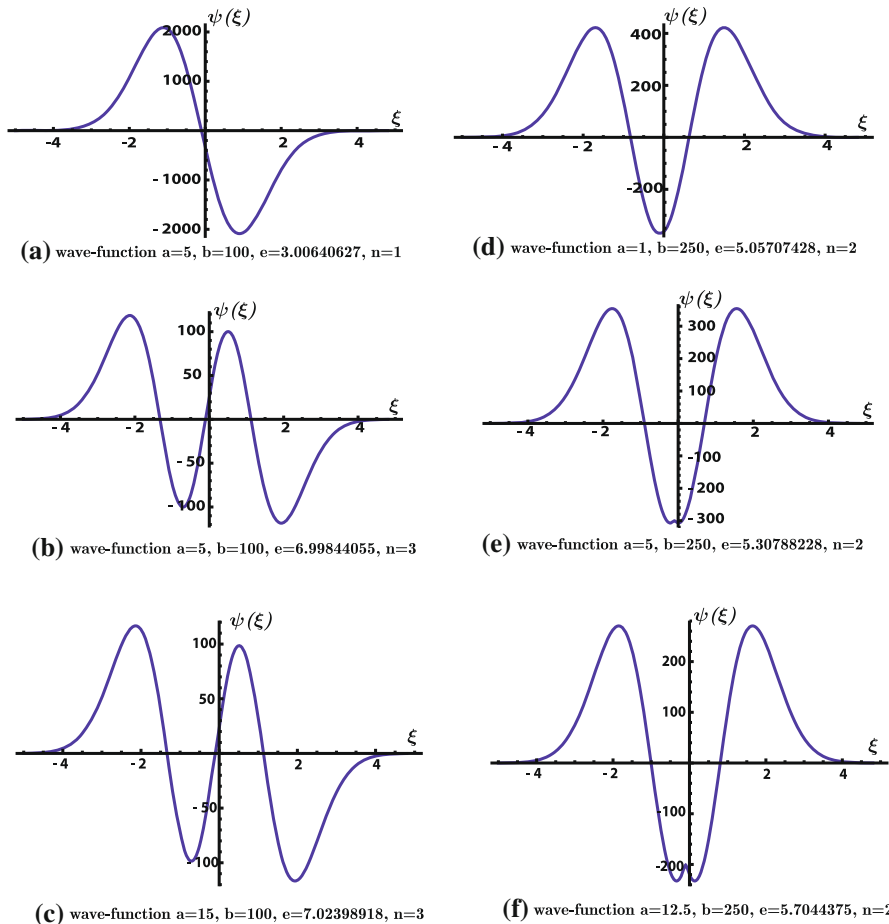**(f)** wave-function a=15, b=500, e=5.3337416.

Fig. 5 Comparison between numerical shooting method wave-function (**a–c**) and perturbation theory wave-function (**d–f**) for second excited-state of a Gaussian symmetric double-well potential

4 Conclusion

The numerical shooting method [11] is generally regarded as one of the most efficient methods that give very accurate results because it integrates the Schrödinger equation directly, though in the numerical sense.

case :1 The Gaussian symmetric double-well potential.

The energy eigenvalue at range 5 ($\xi_{max} = 5$) are in harmony. From Tables 1, 2, 3 and 4 the excited-state energy eigenvalue in case of the numerical shooting method a little is different from the perturbation theory. From Tables 1, 2, 3 and 4 the ground-state energy eigenvalue in case of the numerical shooting method a increase is different

(a) wave-function a=5, b=100, e=3.00640627, n=1

(b) wave-function a=5, b=100, e=6.99844055, n=3

(c) wave-function a=15, b=100, e=7.02398918, n=3

(d) wave-function a=1, b=250, e=5.05707428, n=2

(e) wave-function a=5, b=250, e=5.30788228, n=2

(f) wave-function a=12.5, b=250, e=5.7044375, n=2

Fig. 6 Plot of several functions involving wave-functions of the Gaussian symmetric double-well potential via numerical shooting method. **a–c** Plot of the wave-functions for excited-state ($n = 1, n = 3$) of potential. **d–f** Plot of the wave-functions for excited-state ($n = 2$) and vary barrier ($a = 1$, $a = 5$, $a = 12.5$) of potential

from the perturbation theory. From Table 5, if higher a affect increasing value of energy and %different see Fig. 6d–f. From Tables 1, 2, 3 and 4, if the value of b has increase, the energy eigenvalue (ε) has lessen. Figure 5 shows sketches of the numerical shooting method to perturbation theory wave-functions for second excited-state energy of a Gaussian symmetric double-well potential. The wave-function of a particle whose energy ε is less than the Gaussian symmetric double-well potential barrier height (a). Note that wave-function decays exponentially within region barrier show Fig. 1. The n = even case is shown in Fig. 5. In this case, the wave-function has split up symmetric nodes. The n = odd case is shown in Fig. 6a–c and Fig. 4–18 of the reference [17]. In this case, the wave function similar to in case of a typical harmonic oscillator. If height b or a affect the wave-function has split up increase nodes.

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