Indian J. Phys. **70B** (3), 223–230 (1996)

I J P B
- an international journal

Energy eigenvalues and splitting between even and odd energy levels of a double-well potential

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Received 1 December 1995, accepted 11 April 1996

Abstract : Accurate eigenvalues and splitting ΔE between the even and odd energy levels are calculated for a double-well potential $V(x, Z_x^2, \lambda) = -Z_x^2 x^2 + \lambda x^4$, in the one-dimensional system, using finite difference technique for various values of parameters Z_x^2, λ

Keywords : Schrödinger equation, double-well potential, numerical results and discussion.

PACS No. : 03 65.

1. Introduction

The double-well potential for one-dimensional quantum system has been the subject of intensive study in the last two decades. The literature on this topic, voluminous as it is, has recently been thoroughly referenced by several workers [1–10].

There is a large number of physical and chemical systems whose properties can be studied (modelled) assuming that the potential function responsible for such properties is well represented by means of a function with two valleys and a barrier between them.

Some of the problems to which the double-well potential model has been applied are the interpretation of the infrared spectra of the NH_3 molecule, infrared and Raman spectra of hydrogen-bonded systems, inversion characteristics of isomers, structural phase transitions, formation of noble-gas monolayers on a graphite substrate, macroscopic quantum coherence in super conducting Joseohson devices, and so on [11,12]. In the theory of these problems, the most important characteristics are related to the separation between the two lowest-lying energy levels as it defines the tunnelling rate through the double-well barrier.

The fundamental system of interest to us here is the double-well potential described by Schrödinger equation

$$-\frac{d^2\Psi(x)}{dx} + V(x,; Z_x^2, \lambda)\Psi(x) = E\Psi(x), \tag{1}$$

where $$V(x; Z_x^2, \lambda) = -Z_x^2 x^2 + \lambda x^4. \tag{2}$$

The potential $V(x; Z_x^2, \lambda)$ consist of two potential wells separated by a barrier. If the barrier were impenetrable to a particle, there would be energy levels corresponding to the motion of the particle in one or other well, the same for both well. The fact that a passage through the barrier is possible, results in splitting of each of these levels into two neighbouring ones, corresponding to states in which the particle moves simultaneously in both wells

The eigenvalue spectrum of the Schrödinger eq. (1) with the potential $V(x; Z_x^2, \lambda)$ has the feature that the lower eigenvalues are closely bunched in one group if the values of the Z_x^2 are sufficiently large. As Z_x^2 increases, the magnitude of the splitting between the even and odd energy levels decreases.

In the present work, we have carried out a detailed investigation of the energy eigenvalues of double-well potential over a wide range of Z_λ^2 and λ values. We have achieved our objective using the finite difference. The specific goal we set before us is, to study the splitting between the even and odd energy levels over a wide range of Z_x^2, λ and n_x. It is worth noting here that the finite difference technique is used in this work in the form of combination with a matrix diagonalization for numerical computations and transformed the Schrödinger equation into an algebraic eigenvalue problem.

2. Formulation of the finite difference method

The theory of the finite difference approach to find eigenvalues for the Schrödinger equation with potential given by eq. (2) usually starts from the central difference operator, which can be expressed as

$$\delta = e^{hD/2} - e^{-hD/2} = 2\sinh(hD/2) \tag{3}$$

from eq. (3), it is easy to get

$$h^2D^2 = 4\left[\sinh^{-1}\left[\frac{\delta}{2}\right]\right]^2, \tag{4}$$

where $$\sinh^{-1}\left[\frac{\delta}{2}\right] = \left[\frac{\delta}{2}\right]\left(1 - \frac{1}{6}\left[\frac{\delta}{2}\right]^2 + \frac{3}{40}\left[\frac{\delta}{2}\right]^4 - \frac{5}{112}\left[\frac{\delta}{2}\right]^6 + \frac{35}{1152}\left[\frac{\delta}{2}\right]^8 + \cdots\right). \tag{5}$$

Therefore, eq. (4) takes the following form

$$h^2D^2 = \delta^2 - \frac{\delta^4}{12} + \frac{\delta^6}{90} - \frac{\delta^8}{560} + \frac{\delta^{10}}{3150} - \frac{407\delta^{12}}{24772608} + \frac{493\delta^{14}}{308281344} - \frac{25\delta^{16}}{150994944} + \frac{1225\delta^{18}}{86973087744}, \tag{6}$$

where h is the considered step length and δ applies on function $\Psi(x)$ as follows. Our results show involving the fourth term in eq. (6). The accuracy improves by truncating (6) after the fourth term, giving an overall accuracy of nineteen significant digits.

$$\delta\Psi(x) = \Psi\left(x + \frac{1}{2}h\right) - \Psi\left(x - \frac{1}{2}h\right), \tag{7}$$

$$\delta^2\Psi(x) = \Psi(x+h) - 2\Psi(x) + \Psi(x-h), \tag{8}$$

$$\delta^4\Psi(x) = \Psi(x+2h) - 4[\Psi(x+h) + \Psi(x-h)] + 6\Psi(x) + \Psi(x-2h), \tag{9}$$

$$\delta^2\Psi(x) = \Psi(x+3h) - 6[\Psi(x+2h) + \Psi(x-2h)] + 15[\Psi(x+h) + \Psi(x-h)] - 20\Psi(x) + \Psi(x-3h), \tag{10}$$

$$\delta^8\Psi(x) = \Psi(x+4h) - 8[\Psi(x+3h) + \Psi(x-3h)] + 28[\Psi(x+2h) + \Psi(x-2h)] - 56[\Psi(x+h) + \Psi(x-h)] + 70\Psi(x) + \Psi(x-4h). \tag{11}$$

Although the solutions of (1) are explicitly defined in $(-\infty, +\infty)$, it should be noted that these solutions are either of even or odd parity *i.e.* $\Psi(x) = \pm\Psi(-x)$, so that the determination of $\Psi(x)$ can be restricted to the region $(0, +\infty)$. Furthermore, one can suppose that the wavefunctions are restricted to obey the Dirichlet boundary condition $\Psi(x) = 0$ at some x value R. An acceptable R-value will be guessed numerically.

If we replace D^2 from eq. (6) and using eqs. (7–11), the Schrödinger equation transforms into an algebraic eigenvalue problem of the form

$$\left[C_{m,n} - GI\right]\Psi(nh) = 0, \tag{12}$$

where G is proportional to E and its value $G = -5040\,Eh^2$, I is the unity matrix. The form of matrix associated with eq. (12) can be expressed as

$$\begin{pmatrix} C_{0,0} & C_{0,1} & C_{0,2} & C_{0,3} & C_{0,4} & C_{0,5} & C_{0,6} & C_{0,7} & \cdots C_{0,n} \\ C_{1,0} & C_{1,1} & C_{1,2} & C_{1,3} & C_{1,4} & C_{1,5} & C_{1,6} & C_{1,7} & \cdots C_{1,n} \\ C_{2,0} & C_{2,1} & C_{2,2} & C_{2,3} & C_{2,4} & C_{2,5} & C_{2,6} & C_{2,7} & \cdots C_{2,n} \\ C_{3,0} & C_{3,1} & C_{3,2} & C_{3,3} & C_{3,4} & C_{3,5} & C_{3,6} & C_{3,7} & \cdots C_{3,n} \\ C_{4,0} & C_{4,1} & C_{4,2} & C_{4,3} & C_{4,4} & C_{4,5} & C_{4,6} & C_{4,7} & \cdots C_{4,n} \\ C_{5,0} & C_{5,1} & C_{5,2} & C_{5,3} & C_{5,4} & C_{5,5} & C_{5,6} & C_{5,7} & \cdots C_{5,n} \\ C_{6,0} & C_{6,1} & C_{6,2} & C_{6,3} & C_{6,4} & C_{6,5} & C_{6,6} & C_{6,7} & \cdots C_{6,n} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdots \\ \cdot & & & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot C_{m,n} \end{pmatrix} \begin{pmatrix} \Psi(0) \\ \Psi(h) \\ \Psi(2h) \\ \Psi(3h) \\ \Psi(4h) \\ \Psi(5h) \\ \Psi(6h) \\ \\ \\ \Psi(nh) \end{pmatrix} = 0.$$

The values of some coefficients are given below

$$C_{0,0} = \gamma_0 - G, \quad \text{where} \quad \gamma_n = -5040\left[\frac{205}{72} - h^2 V(nh)\right],$$

$C_{0,1} = 161268$, $C_{0,2} = 2016$, $C_{0,3} = 256$, $C_{0,4} = -18$,

$C_{0,5} = 0$, $C_{0,6} = 0$, $C_{1,0} = 8064$, $C_{1,1} = \mu_1 + \gamma_1 - G$,

$\mu_1 = \mp 1008$, $C_{1,2} = 8064 \pm 128$, $C_{1,3} = 1008 \mp 9$, $C_{1,4} = 128$,

$C_{1,5} = -9$, $C_{1,6} = 0$, $C_{2,0} = -1008$, $C_{2,1} = C_{1,2}$,

$C_{2,2} = \mu_2 + \gamma_2 - G$, $\mu_2 = \mp 9$, $C_{2,3} = 8064$, $C_{2,4} = -1008$,

$C_{2,5} = 128$, $C_{2,6} = -9$, $C_{3,0} = 128$, $C_{3,1} = -1008 \mp 9$,

$C_{3,2} = 8064$, $C_{3,3} = \gamma_3 - G$, $C_{3,4} = 8064$, $C_{3,5} = -1008$,

$C_{3,6} = 128$, $C_{3,7} = -9$, $C_{3,8} = 0$, $C_{4,0} = -9$,

$C_{4,1} = 128$, $C_{4,2} = -1008$, $C_{4,3} = 8064$, $C_{4,4} = \gamma_4 - G$,

$C_{4,5} = 8064$, $C_{4,6} = -1008$, $C_{4,7} = 128$, $C_{4,8} = -9$,

$C_{4,9} = 0$, $C_{5,0} = 0$, $C_{5,1} = -9$, $C_{5,2} = 128$,

$C_{5,3} = -1008$, $C_{5,4} = 8064$, $C_{5,5} = \gamma_4 - G$, $C_{5,6} = 8064$,

$C_{5,7} = -1008$, $C_{5,8} = 128$, $C_{5,9} = -9$, $C_{5,10} = 0$,

$C_{5,11} = 0$.

It should be noted that the double sign ($\mp$), which appear in some coefficients above, which mean, the states with even parity take (+) and states with odd parity take (−). Also it should be mentioned that for even parity states the coefficients $C_{0,n}$, ($n \geq 1$), become zero.

To solve the algebraic eigenvalue problem for eq. (12), we first transform the matrix $C_{m,n}$ to a symmetric one. Due to the already special form of $C_{m,n}$ this can be done by means of one similarity transformation. We then reduce this matrix to a tridiagonal form by preliminary transformations. To calculate eigenvalues of this symmetric tridiagonal matrix, we use the F02BEF Subroutine of the NAG-Library [13]. To select out the correct energy we require stability of our results with respect to the small variation of R at a given value of step length h.

3. Results and discussion

The finite difference technique has been applied in this paper for a double-well potentials in one dimensional system. Eigenvalues for different values of Z_x^2, λ and state numbers n_x are listed in the Tables 1 and 2.

Table 1. Ground- and first-excited state energies for a double-well potential $V(x, Z_x^2, \lambda = 1)$, for different values of Z_x^2 $E_{n_x}^{\text{ref}}$ (other) represents other values.

Z_x^2	n_x	E_{n_x} (present)	$E_{n_x}^{\text{ref}}$ (other)
0	0	1.060362090484182	1.0606209048^4
	1	3.799673029801394	3.7997302980^4
0.5	0	0.870017518371612	0.8700175183^{72}
	1	3.333779329887006	3.3337793298^9
1	0	0.657653005180715	0.6576530051^{91}
	1	2.834536202119304	2.8345362021^2
2	0	0.137785848188222	0.1377858481882225^5
	1	1.713027897767675	1.7130278977676^5
4	0	-1.710350450132638	-1.7103504501326^{40}
	1	-1.247922492066213	-1.2479224920662^{15}
5	0	-3.410142761239829	-3.4101427612398^{30}
	1	-3.250675362289235	-3.2506753622892^{36}
25	0	-149.219456142190888	-149.219456142191^3
	1	-149.219456142190888	-149.219456142191^0
50	0	-615.020090902757816	-615.020090902757^6
	1	-615.020090902757816	-615.020090902757^6
100	0	-2845.867880342075294	-2845.867880342076^6
	1	-2845.867880342075294	-2845.867880342076^6
200	0	-9980.005002815982695	-9980.0050028159826956^7
	1	-9980.005002815982695	-9980.005002815982695^7

As suggested by the referee, comparison with the results of other methods [4–7] has been made in Tables 1 and 2. It is clear from Tables 1 and 2 that there is agreement between our results and the results produced by other methods.

In Table 1, we compare the results obtained by the present method with those obtained by other methods [4–7]. The values of the energy are calculated over a wide range of $0 \leq Z_t^2 \leq 200$ at $\lambda = 1$, for the ground and first-excited state. As Z_x^2 increases, the magnitude of the splitting between the energy levels for ground and first-excited state $|E_0 - E_1|$ decreases.

In Table 2, we compare the results obtained by our method with those obtained by using power series method for two values of $Z_x^2 = 10$, 100 and $\lambda = 0.5$, 7.5. Generally speaking, the agreement between our values and those of power series is very good. Some

Table 2. Numerical values of some energy eigenvalues for the double-well potential $V(x, Z_t^2, \lambda)$

Z_t^2	λ	n_x	Present method	Power series method
		0	−45 5791974486965547	−45.57919744869655473
		1	−45.5791974486818590	−45.57919744868185901
		2	−36 9538380723252171	−36.95383807232521710
		3	−36 9538380677618931	−36 95383806776189305
		4	−28.6830875222325604	−28.68308752223256042
		5	−28 6830868969642709	−28.68308689696427091
10	0 5	12	−1.4089110509977329	−1 40891105099773294
		13	−0 5217551377821886	−0 52175513778218866
		16	8 9976916989575165	8.99769169895754647
		17	12 5121782111944881	12.51217821119448815
		18	16 2532388098463624	16.25323880984636237
		19	20 1747735655636969	20 17477356556369698
		0	−319 2671170279540906	−319 26711702795409060
		1	−319 2671170279540906	−319 26711702795409060
		2	−291.4454394228711989	−291.44543942287119896
		3	−291.4454394228711989	−291.44543942287119896
		4	−264.1075745401302216	−264.10757454013022166
		5	−264.1075745401302216	−264.10757454013022166
		6	−237 2797814701336811	−237.27978147013368111
		7	−237 2797814701336811	−237 27978147013368111
		8	−210.9923806353957530	−210 99238063539575303
		9	−210.9923806353957506	−210 99238063539575069
		10	−185 2808776964343650	−185 28087769643436504
100	7.5	11	−185.2808776964341016	−185.28087769643410164
		24	−27 0044852236812682	−27 00448522368126821
		25	−26.9211476446426514	−26.92114764464265145
		26	−10 0772932133725591	−10.07729321337255916
		27	−8.9598963608357662	−8.95989636083576627

Table 2. *(Cont'd.)*

Z_x^2	λ	n_x	Present method	Power series method
		28	2.7350408154161046	2.73504081541610463
		29	8.1915969606041077	8.19159696060410771
		30	17.4123343420860030	17 41233434208600301
		31	26.2920453927462065	26.29204539274620650
		32	36 0236079545425696	36.02360795454256961
		33	46.1417178714088725	46.14171787140887259

fine points, however may be noted, as Z_x^2 increases, the energy levels for states of even and odd parity become effectively degenerate *i.e.* $E_{even} = E_{odd}$. The splitting increases rapidly as one goes to higher levels.

To show the dependence of the results on the choice of the R value, we present in Table 3 again for $Z_x^2 = 10$ and $\lambda = 0.5$, the results obtained with step length $h = 1/20$ but

Table 3. The dependence of the results on the choice of the R value

Z_x^2	λ	n_x	E_{n_x}	R	h
10	0.5	1	−45.357 148 594 361 401 06	4	1/20
			−45.579 197 233 453 902 44	5	
			−45.579 197 448 681 859 01	6	
			−45.579 197 448 681 859 01	7	
			−45.579 197 448 681 859 01	8	
			−45.579 197 448 681 859 01	10	

with six different R values, *i.e.* $R = 4, 5, 6, 7, 8$ and 10. Our results in Table 3 do not change anymore whenever $R \geq 5$. Of course one should control for each parameters (Z_x^2, λ) choice the influence of the chosen R value on the results.

Acknowledgment

The author is grateful to the referee for his valuable comments and suggestions in the light of which this paper has been revised.

This research was supported in part by a research grant No. GR/K17750 from the Engineering and Physical Science Research Council.

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