

One-dimensional multiple-well oscillators: A time-dependent quantum mechanical approach

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MS received 24 June 2002

Abstract. Time-dependent Schrödinger equation (TDSE) is solved numerically to calculate the ground- and first three excited-state energies, expectation values $\langle x^{2j} \rangle$, $j = 1, 2, \dots, 6$, and probability densities of quantum mechanical multiple-well oscillators. An imaginary-time evolution technique, coupled with the minimization of energy expectation value to reach a global minimum, subject to orthogonality constraint (for excited states) has been employed. Pseudodegeneracy in symmetric, deep multiple-well potentials, probability densities and the effect of an asymmetry parameter on pseudodegeneracy are discussed.

Keywords. Multiple-well oscillators; time-dependent quantum mechanics.

PACS Nos 03.65.-w; 03.65.Ge; 02.70.-c; 05.10.Ln; 05.45.-a

1. Introduction

The aim of this paper is to calculate the eigenvalues of general quantum multiple-well oscillators described by the Hamiltonian (atomic units employed throughout)

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

where

$$V(x) = \pm \frac{1}{2} \omega^2 x^2 + \sum_{i=2}^N a_{2i} x^{2i}, \quad a_{2i} \text{ real.} \quad (2)$$

The last two decades have seen significant developments in theoretical studies of quantum mechanical anharmonic oscillators which offer interesting mathematical and computational challenges. Various methods of approximation and numerical techniques have

been proposed to calculate the energy eigenvalues of anharmonic oscillators (AHO) and double-well oscillators (DWO) [1–13]. However, only limited investigation has been carried out on multiple-well oscillators (MWO) [14,15]. The MWO are relevant in the study of resonant tunneling transistors [16], oscillatory chemical reactions [17], the adsorption of atoms/molecules on a solid substrate, etc.

Earlier attempts to calculate the energy eigenvalues of MWO employed approximations to the time-independent Schrödinger equation (TISE) [14,15]. The time-dependent quantum mechanical approach is employed here for the first time to calculate the energy eigenvalues, expectation values $\langle x^{2j} \rangle$ ($j = 1, 2, \dots, 6$) and probability densities of the ground state and the first three excited states of one-dimensional MWO. We also investigate the deep multiple-well potentials that lead to pseudodegenerate (almost degenerate) energy levels [18]. Previously, pseudodegenerate energy levels for only deep DW potentials were reported by other workers [19–21].

The present work employs essentially a diffusion quantum Monte Carlo method, based on propagating the time-dependent Schrödinger equation (TDSE) in imaginary time coupled with the minimization of energy expectation value, maintaining the orthogonality constraint between states. The computations were carried out in quadruple precision (up to 33 decimal digits using DEC-FORTRAN-90 compiler) although the results are reported up to the digits for which stability was the best. Note that the present methodology is exact in principle and works very well for general quantum mechanical AHO, DWO [22,23] and self-interacting oscillators [24].

Section 2 briefly describes the methodology of computing eigenstates of MWO by transforming the TDSE into a diffusion-type equation by assuming the validity of TDSE in imaginary time. Section 3 presents the results.

2. Methodology

One-dimensional TDSE is

$$H\Psi(x,t) = i\frac{\partial\Psi(x,t)}{\partial t}, \quad (3)$$

where the Hamiltonian H is given by eq. (1). One can obtain a diffusion-type equation similar to the random-walk quantum Monte Carlo equation [25] by first assuming the validity of eq. (3) in imaginary time τ and then replacing τ by $-it$, where t is real time. Replacing the wave function $\Psi(x,t)$ in eq. (3) by a diffusion function $R(x,t)$ transforms the TDSE into a nonlinear diffusion-type equation

$$HR(x,t) = -\frac{\partial R(x,t)}{\partial t}. \quad (4)$$

In the diffusion quantum Monte Carlo (DQMC) approach, the evolution of a classical diffusion-type equation in real time up to a sufficiently long time eventually reaches a stationary ground state corresponding to the globally minimum value of $\langle R(x,t)|H|R(x,t) \rangle$. One can then calculate the successive higher eigen energies by following the same imaginary time evolution but additionally requiring that an excited state is orthogonal to all the lower states. Indeed, one can write [25]

$$R(x,t) = C_0\phi_0(x) + \sum_{i=1}^{\infty} C_i\phi_i(x)e^{-(E_i-E_0)t}, \quad (5)$$

where ϕ_i is a solution of TISE with energy eigenvalue E_i and $\{C_i\}$ are linear TI coefficients; ϕ_0 and E_0 refer to the ground state. Thus, as $t \rightarrow \infty$, $R(x,t) \rightarrow \phi_0$ taking due account of normalization. Equation (5) indicates that at any non-zero finite time, $R(x,t)$ is a linear combination of TISE eigenfunctions $\{\phi_i\}$ with TD coefficients which decay exponentially in real time. The probability density is R^2 while other expectation values can be obtained as $\langle R|A|R\rangle$, R being a minimum-energy (ground or excited) diffusion function and A an operator.

Earlier, the DQMC method of transforming the TDSE into a diffusion equation has been employed to determine the energies of atomic [26] and molecular systems [27] as well as the ground-state energy of a quartic oscillator [28]. However, the calculation of ground and excited states of MWO as well as the calculation of $\langle x^{2j} \rangle$ values with high accuracy by this approach appears to be new.

The numerical method [23] employed here originated from the TD quantum fluid density functional theory (QFDFT) developed in our laboratory. It has been successfully applied to study ground states of atoms and molecules [29,30] as well as ground and excited states of AHO, DWO [23] and self-interacting oscillators [24]. The formal solution of eq. (4) is recast into a tridiagonal matrix equation by using a finite-difference method. The matrix equation is then solved to obtain the function R using a modified Thomas algorithm [31].

The accuracy of the present algorithm has been established by comparing our results for the three- and four-well oscillator for selected values of the parameters ω and a_{2i} in eq. (2) with the literature values [14,15]. Our results are in perfect agreement with these values obtained by using analytical or numerical solutions of the TISE.

3. Results and discussion

Tables 1 and 2 give the energy eigenvalues, expectation values $\langle x^{2j} \rangle$ ($j = 1, 2, \dots, 6$) for the ground state and the first three excited states of symmetric three-, four- and five-well oscillators. When ω^2 is large (deep well) and energy levels lie close to the minima of the well, energy eigenvalues show two-fold pseudodegeneracy (note that one-dimensional potentials do not exhibit degeneracy in any energy eigenvalue [18]). The origin of pseudodegeneracy in multiple-well potentials is not yet clear; in case of double-well potentials, supersymmetric quantum mechanics has been used to find the energy difference between the closely spaced energy levels [21]. The highest order of pseudodegeneracy observed is two-fold. For most of the results reported here, only the ground and the first excited state are pseudodegenerate because as the higher levels approach the barrier, pseudodegeneracy splits up. Figure 1 shows the probability density plots for a three-well potential with two-fold pseudodegeneracy up to the third excited state. The probability density plots for pseudodegenerate eigenstates are nearly identical. Such plots are counter-intuitive.

Table 3 reports the effect of adding an asymmetry term (a_3x^3) in the symmetric even-potential with pseudodegeneracy in the ground and first excited state. The asymmetry term splits the pseudodegeneracy and the energy difference between the initially pseudodegenerate energy levels increases linearly with increasing coefficient of asymmetry. Furthermore, except the second, the other three energy levels are progressively depressed.

Table 1. The energy eigenvalues and $\langle x^{2j} \rangle$ values (in a.u.) of three-, four-, and five-well oscillators. n is the vibrational quantum number.

No. of wells	n	Energy	$\langle x^2 \rangle$	$\langle x^4 \rangle$	$\langle x^6 \rangle$	$\langle x^8 \rangle$	$\langle x^{10} \rangle$	$\langle x^{12} \rangle$
$\omega^2 = 2.64, a_4 = -3.6875, a_6 = 0.5, a_8 = -0.5, a_{10} = 0.5$								
3	0	-0.097561029859 (-0.0975610298673 ^a)	0.6161147	0.6882060	0.9522032	1.496652	2.575338	4.753764
	1	0.562500000017 (0.562500000000 ^a)	0.9568417 (0.9568 ^b)	1.194350 (1.1944 ^b)	1.738359 (1.7384 ^b)	2.813402 (2.8134 ^b)	4.935042 (4.9350 ^b)	9.235111
	2	2.82307176209 (2.823071762068 ^a)	0.7010386	1.022982	1.669871	2.921778	5.417777	10.56743
	3	6.1923733374 (6.19237337299 ^b)	0.7700569	1.133165	1.987085	3.734141	7.351888	15.05919
$\omega^2 = 12.0, a_4 = -2.1, a_6 = 0.18$								
3	0	1.57354821071	0.214150	0.265505	0.939444	4.863962	28.73282	181.6096
	1	2.45260995748	5.096746	28.14096	164.6940	1011.255	6472.073	42971.18
	2	2.47115208354	5.122936	28.42810	166.7957	1025.749	6571.906	43669.18
	3	4.356004520	0.888868	2.402021	12.25322	77.20003	522.7131	3672.419
$\omega^2 = 12.2, a_4 = -1.9, a_6 = 0.16$								
3	0	1.61390884708	0.173927	0.103052	0.124045	0.266751	0.893569	3.980657
	1	4.41392612203	1.080151	2.978788	12.83620	66.99439	386.7673	2386.996
	2	5.15774999293	4.310323	21.62411	118.4832	693.1324	4275.125	27578.22
	3	5.401058843	4.261358	22.49874	127.5864	763.4372	4784.059	31228.74
$\omega^2 = 56.0, a_4 = -14.0, a_6 = 0.1, a_8 = -0.005, a_{10} = 0.15$								
3	0	3.52131271172	0.079828	0.025218	0.023372	0.044662	0.113178	0.318434
	1	6.14440000460	2.502690	6.613766	18.22277	52.00960	153.0922	463.2392
	2	6.15843881825	2.512248	6.649953	18.33630	52.35690	154.1610	466.5769
	3	10.02756555	0.302085	0.245884	0.457232	1.220166	3.650701	11.41715
$\omega^2 = -1.0, a_4 = 1.5, a_6 = -1.0, a_{10} = 0.05$								
4	0	-0.048145973110 (-0.04814597329 ^a)	1.070888	2.088153	4.978417	13.30335	38.46573	118.1340
	1	0.336496621382 (0.336496619391 ^a)	1.699199	3.703997	9.265608	25.42545	74.76713	232.3348
	2	1.55551116437 (1.55551116914 ^b)	1.226552	3.049165	8.393077	24.54263	75.44376	242.1994
$\omega^2 = -7.0, a_4 = 3.4, a_6 = -0.909, a_8 = 0.07$								
4	0	-0.360223631680	1.760163	7.139621	36.40120	204.2616	1212.295	7490.723
	1	-0.102958470502	4.001311	19.92215	108.9854	631.3470	3814.362	23841.96
	2	0.242368272869	3.645746	19.64363	112.5289	670.1510	4123.312	26110.13
$\omega^2 = -11.90, a_4 = 3.96, a_6 = -0.855, a_8 = 0.055$								
4	0	-3.72336651474	6.239637	40.85352	277.4051	1941.505	13949.78	102601.2
	1	-3.72306978179	6.242571	40.87663	277.5731	1942.724	13958.74	102668.1
	2	-1.42355621944	1.174086	3.074593	14.13840	88.63726	632.9348	4775.579
$\omega^2 = -15.4, a_4 = 4.30, a_6 = -0.802, a_8 = 0.0476$								
4	0	-2.73383293068	1.634905	4.276901	15.54608	72.03163	394.4934	2415.843
	1	-2.62188347178	1.842649	5.095140	19.26823	91.76519	511.6857	3170.079
	2	-0.79076173540	3.927897	22.34560	138.4291	905.5523	6185.373	43801.98
$\omega^2 = 2.0, a_4 = -3.75, a_6 = 2.75, a_8 = -0.4385, a_{10} = 0.02$								
5	0	0.403870823605 (0.403870823604 ^a)	0.3893060	0.3599603	0.468432	0.7505087	1.396255	2.920994
	1	1.63897315578 (1.638973155785 ^a)	0.8169086	0.9662356	1.431773	2.492352	4.918995	10.76577
	2	3.83374024806 (3.833740248058 ^a)	0.9025381	1.389383	2.455366	4.837968	10.47868	24.67944

^aRef. [14]; ^bref. [15].

Table 2. The energy eigenvalues and $\langle x^{2j} \rangle$ values (in a.u.) of symmetric three-well potentials with pseudodegenerate energy levels. n is the vibrational quantum number.

n	Energy	$\langle x^2 \rangle$	$\langle x^4 \rangle$	$\langle x^6 \rangle$	$\langle x^8 \rangle$	$\langle x^{10} \rangle$	$\langle x^{12} \rangle$
$\omega^2 = 17.0, a_4 = -2.5, a_6 = 0.16$							
0	-5.45558636501	7.868207	63.66301	528.5273	4493.773	39069.18	346854.4
1	-5.45558636243	7.868207	63.66301	528.5273	4493.772	39069.17	346854.4
2	1.93817745261	0.142523	0.080011	0.180271	1.158017	10.09047	95.52287
$\omega^2 = 20.8, a_4 = -2.1, a_6 = 0.1$							
0	-1.87232824968	10.36682	109.7377	1184.613	13026.45	145774.3	1658687.7
1	-1.87232824961	10.36682	109.7377	1184.613	13026.45	145774.2	1658687.6
2	2.20010372642	0.118383	0.043373	0.027450	0.025487	0.033448	0.0729041
3	6.420362405	0.382254	0.273168	0.476101	0.476101	30.93778	370.9178
$\omega^2 = 78.0, a_4 = -24.0, a_6 = 1.8, a_8 = -0.07, a_{10} = 0.05$							
0	-66.9864755976	4.214371	18.02648	78.20300	343.8663	1531.636	6907.016
1	-66.9864755976	4.214371	18.02648	78.20300	343.8663	1531.636	6907.016
2	-36.6227680686	3.870597	15.77727	67.46962	300.9010	1389.895	6604.775
$\omega^2 = 27.0, a_4 = -1.5, a_6 = 0.035$							
0	-50.7484721234	22.68810	518.3336	11922.67	276079.0	643478903	150946625.3
1	-50.7484721234	22.68810	518.3336	11922.67	276079.0	6434789.3	150946624.6
2	-38.2485435620	22.08645	498.5468	11491.98	270165.6	6466824.7	157315608.4
3	-38.24854356	22.08645	498.5468	11491.98	270165.6	6466823.5	157315574.5

Table 3. Effect of asymmetry (a_3 parameter) on pseudodegeneracy in symmetric three-well potentials, n is the vibrational quantum number (the computations were executed in double precision).

ω^2	a_3	a_4	a_6	n	Energy	$\Delta E = E_1 - E_0$
17.0	0.001	-2.5	0.16	0	-5.47789101	0.04461048
				1	-5.43328053	
				2	1.93817761	
				3	2.91621648	
17.0	0.002	-2.5	0.16	0	-5.50020845	0.08922439
				1	-5.41098406	
				2	1.93817724	
				3	2.89775697	
17.0	0.004	-2.5	0.16	0	-5.54486345	0.17845048
				1	-5.36641297	
				2	1.93817568	
				3	2.86079951	
17.0	0.008	-2.5	0.16	0	-5.63425677	0.35690152
				1	-5.27735525	
				2	1.93816925	
				3	2.78675614	
17.0	0.032	-2.5	0.16	0	-6.17295372	1.42758295
				1	-4.74537077	
				2	1.93797582	
				3	2.33912596	
17.0	0.128	-2.5	0.16	0	-8.36729378	5.70877493
				1	-2.65851885	
				2	0.49060396	
				3	1.9383794	

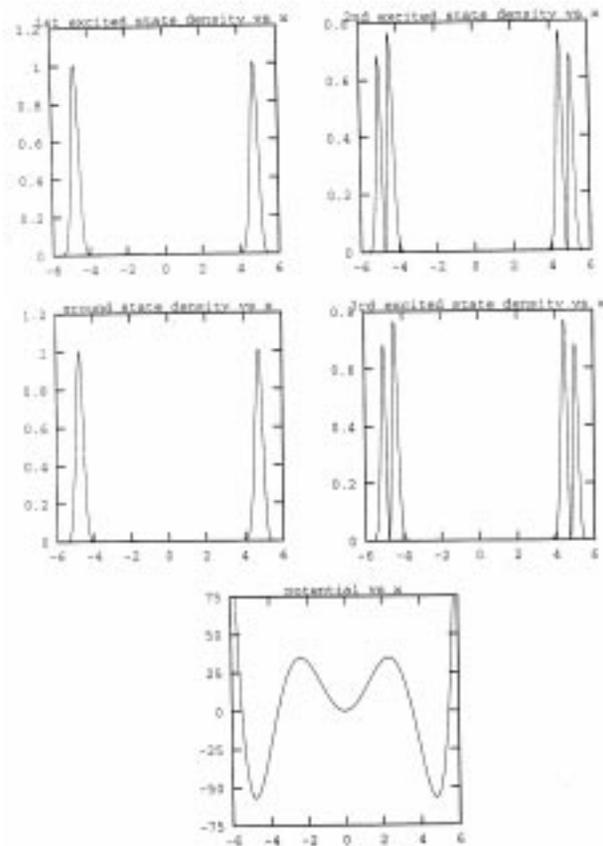


Figure 1. Potential energy and probability density plots (a.u.) for the symmetric three-well oscillator, governed by the potential (table 2), $V(x) = 13.5x^2 - 1.5x^4 + 0.035x^6$.

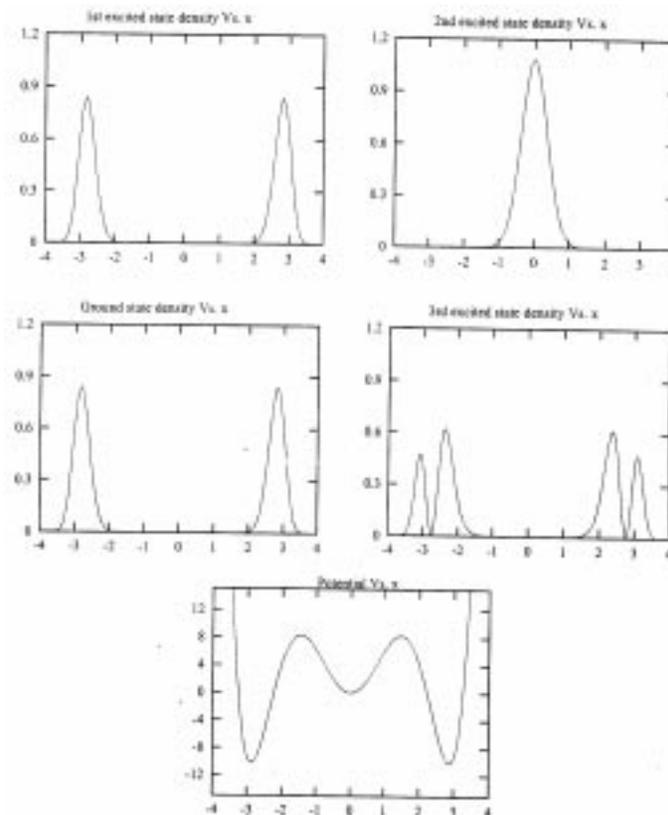


Figure 2. Potential energy and probability density plots (a.u.) for the symmetric three-well oscillator, governed by the potential (table 2), $V(x) = 8.5x^2 - 2.5x^4 + 0.16x^6$.

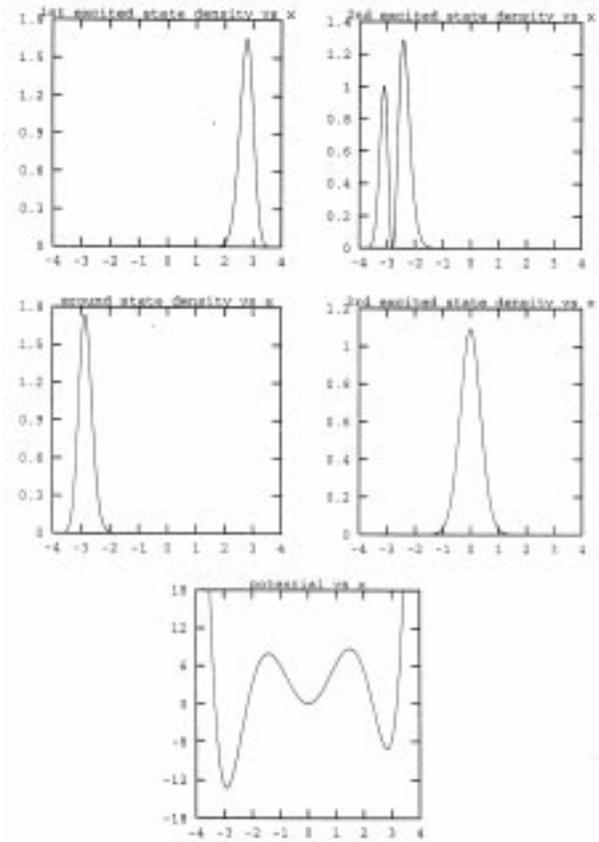


Figure 3. Potential energy and probability density plots (a.u.) for the asymmetric three-well oscillator, governed by the potential (table 3), $V(x) = 8.5x^2 + 0.128x^3 - 2.5x^4 + 0.16x^6$.

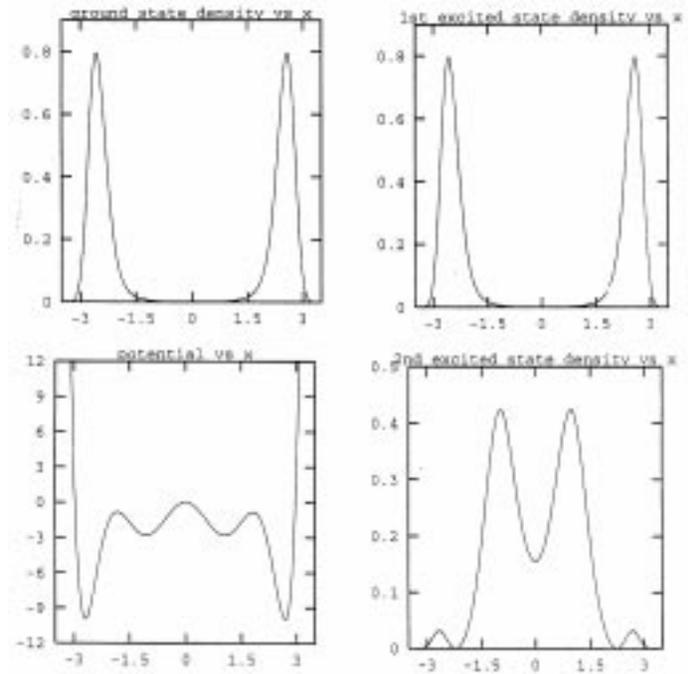


Figure 4. Potential energy and probability density plots (a.u.) for the symmetric four-well oscillator, governed by the potential (table 1), $V(x) = -5.95x^2 + 3.96x^4 - 0.855x^6 + 0.055x^8$.

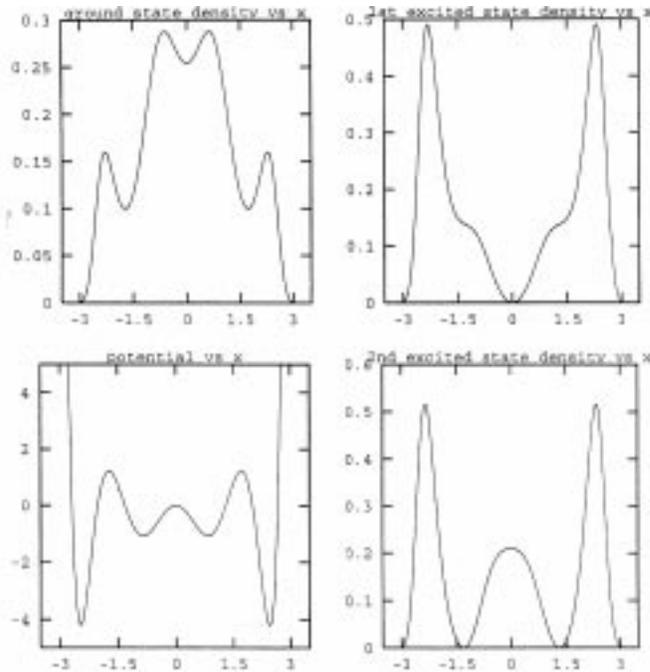


Figure 5. Potential energy and probability density plots (a.u.) for the symmetric four-well oscillator, governed by the potential (table 1), $V(x) = -3.5x^2 + 3.4x^4 - 0.909x^6 + 0.07x^8$.

The probability density plots for two potentials in table 3 are depicted in figures 2 and 3. For pseudodegenerate ground- and first-excited states, the plots in figure 2 show two equal peaks corresponding to the deeper side wells. The next higher states remain orthogonal to all the lower states while keeping the number of nodes at a minimum in order to reduce energy. It is obvious that symmetric potentials must lead to symmetric probability density plots. Figure 3 shows the effect of asymmetry incorporated in a symmetric three-well potential. Since the asymmetry term acts as a perturbation to split the pseudodegeneracy in a symmetric three-well potential, the wave function for the perturbed potential are linear combinations of the wave functions of the unperturbed potential. This explains the single peaks in the ground- and the first-excited state probability density plots (figure 3). The higher states do not appear in the linear combination due to a large energy difference. Interestingly, the single-peak density corresponding to an energy of ~ 1.94 a.u. (table 3) occurs in figures 2 and 3.

Figure 4 shows the probability density plots for a four-well potential with pseudodegeneracy in the ground- and first-excited state. As expected, pseudodegenerate states show nearly identical plots. Figure 5 gives the plots for a four-well potential without any pseudodegenerate eigenstate. These probability density plots are faithful to intuition and have the expected nodal structure. The present results may be helpful for understanding time-dependent phenomena where a multiple-well potential energy curve/surface pulsates in time and thereby controls a particular process.

Acknowledgement

The authors (AKR) and (NG) thank the Council of Scientific and Industrial Research, New Delhi, for financial support.

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