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Energy Levels for Nonsymmetric Double-Well Potentials in Several Dimensions: Hill Determinant Approach

M. R. M. WITWIT

Department of Applied Mathematics, University of Hull, Hull, HU6 7RX, United Kingdom

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Energy levels for double-well potentials in one-, two-, and three-dimensional systems are calculated using the Hill determinant approach for several eigenstates and large values of the perturbation parameters ($\lambda, Z_x^2, Z_y^2, Z_z^2$). Numerical results for some special cases agree with those of previous workers where available.

1. INTRODUCTION

The double-well potential for one-dimensional quantum systems [1–11] has been the subject of numerous investigations, and the corresponding literature is consequently, quite extensive. Although various aspects of the problem have been the subject of much interesting work, both from the analytical and the numerical point of view, comparable investigations have not been carried out in the case of multidimensional systems [12].

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.

Examples of such potentials occur in the study 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 Josephson devices, and so on [13–14]. 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.

In this work, the general form of Schrödinger equation for the double-well potential in several dimensions system can be written as

$$\left[-\sum_{I=1}^{d}\frac{\partial^2}{\partial x_I^2}+V_d(x_I,...;Z_{x_I}^2,...,\lambda)\right]\Phi(x_I,...)=E\Phi(x_I,...) \tag{1}$$

$$(x_1=x, x_2=y, x_3=z).$$

Here, and subsequently, all the indices run over 1, 2, 3, so that the coordinate x_I runs over x, y, and z. The notation $d = 1, 2$, or 3 refers to the number of dimensions, λ is a positive perturbation parameter, and Z_x^2, Z_y^2, Z_z^2 refer to the depth of the potential well.

The solution of the Schrödinger equation for a nonsymmetric double well in two and three dimensions has not received the attention it deserves. This is unfortunate because there have been misconceptions in the literature regarding the effect of two unequal minima in potential functions on the infrared and Raman spectra of hydrogen-bonded systems [13].

In the present paper, the Hill determinant approach is applied to three examples: the double-well potential in one dimension,

$$V_1(x;Z_x^2,\lambda)=-Z_x^2x^2+\lambda x^4 \tag{2}$$

in two-dimensions,

$$V_2(x,y;Z_x^2,Z_y^2,\lambda)=-Z_x^2x^2-Z_y^2y^2+\lambda[a_{xx}x^4+2a_{xy}x^2y^2+a_{yy}y^4], \tag{3}$$

and in three-dimensions,

$$\begin{aligned}V_3(x,y,z;Z_x^2,Z_y^2,Z_z^2,\lambda)&=-Z_x^2x^2-Z_y^2y^2-Z_z^2z^2+\lambda[a_{xx}x^4+a_{yy}y^4+a_{zz}z^4\\&\quad+2a_{xy}x^2y^2+2a_{xz}x^2z^2+2a_{yz}y^2z^2].\end{aligned} \tag{4}$$

The potentials $V_1(x;Z_x^2,\lambda), V_2(x,y;Z_x^2,Z_y^2,\lambda)$, and $V_3(x,y,z;Z_x^2,Z_y^2,Z_z^2,\lambda)$ 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 the other well, the same for both wells. The fact that a passage through the barrier is possible results in the splitting of each of these levels into two neighboring ones, corresponding to states in which the particle moves simultaneously in both wells.

The depth of the double well is controlled by the parameters Z_x^2, Z_y^2, Z_z^2, and λ (see Figs. 1, 2). The Hill determinant

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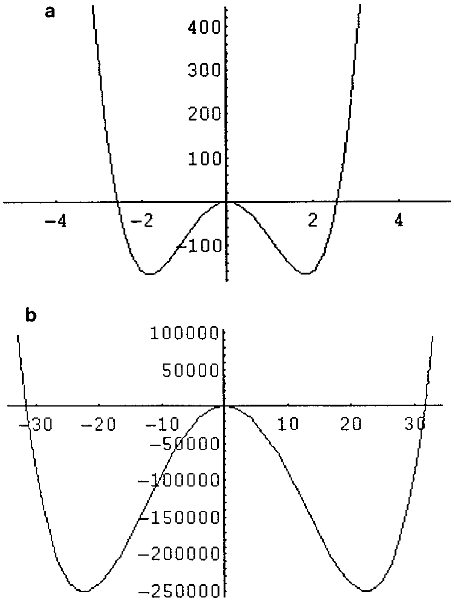

FIG. 1. a. Double-well potential $V_1(x; Z_x^2 = 10, \lambda = 1)$; b. Double-well potential $V_1(x; Z_x^2 = 1000, \lambda = 1)$.

approach works well for small and medium values of Z_x^2, Z_y^2, Z_z^2 at low values of λ; as Z_x^2, Z_y^2, and Z_z^2 increase the depth of the well increases and for a deep well the convergence decreases.

Physically, when the potential well is very deep (for large Z_x^2, Z_y^2, Z_z^2 values) the classical turning points for the lowest bound states are very close to the minimum of each well; therefore the particle, even quantum mechanically, can in the main see only the region of the potential near the minima. The lower levels for this potential have therefore very nearly degenerate eigenvalues.

When $Z_x^2 = Z_y^2 = Z_z^2 = Z^2$, the potentials in two and three dimensions have rotation symmetry, which makes it easier to handle the calculations. We should comment here that handling potential functions with symmetric behaviour is preferable, because it is simpler and their computation is more quickly performed than nonsymmetric behaviour and requires less memory.

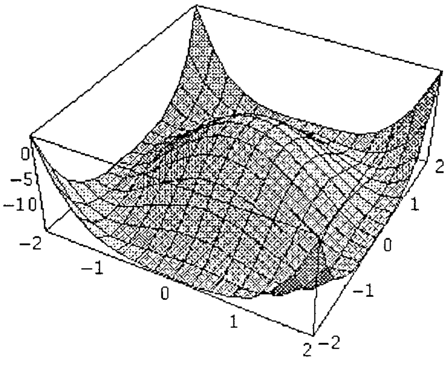

FIG. 2. Double-well potential $V_2(x, y; Z_x^2 = Z_y^2 = 7.5, \lambda = 1)$.

The eigenvalue spectrum of the Schrödinger equation (1) with $V_d(x_I, ...; Z_{x_I}^2, ..., \lambda)$ has the feature that the lower eigenvalues are closely bunched in one group if the values of the Z's are sufficiently large. As Z_x^2, Z_y^2, and Z_z^2 increase, the magnitude of the splitting between these levels decreases; i.e.,

$$|E_1 - E_0| = \Delta E_{d=1} \cong 0 \tag{5}$$

$$|E_{11} - E_{00}| \approx |E_{11} - E_{10}| = \Delta E_{d=2} \cong 0 \tag{6}$$

$$|E_{111} - E_{000}| \approx |E_{000} - E_{100}| \approx |E_{100} - E_{110}| = \Delta E_{d=3} \cong 0. \tag{7}$$

The splitting ΔE will be small at the bottom of the well and will increase as the levels approach the top of the barrier. When ΔE_d has its minimum value, the nearly degenerate eigenfunctions have equal weight in each potential well.

The double-well potential given by Eq. (1) in two and three dimensions is, in general, nonseparable in Cartesian coordinates, showing nonsymmetrical behaviour and, due to this behaviour, requires a great deal of computation to arrive at our results.

The paper is organized as follows. Section one is concerned with the Hill determinant approach and its use to calculate the energy eigenvalues for the double-well potentials in one, two, and three dimensions for several eigenstates. Section 4 contains a discussion of the results.

2. THE HILL DETERMINANT APPROACH

The Hill determinant approach is a nonperturbative technique used to treat the perturbed oscillator problem in one, two, and three dimensions. Much of the traditional literature on Hill determinants deals with one-dimensional problems [15–31]; the extension to two or three dimensions necessarily involves the use of a product basis set, leading to large matrix or determinant problems, which are conveniently handled by a relaxation method.

However, despite the success of the Hill determinant approach in calculating energy eigenvalues there has been some theoretical debate [18, 19] about the question of whether it can give "false" eigenvalues which do not correspond to normalizable wavefunctions. The difficulties originally encountered by Flessa [18, 19] in connection with application of the Hill determinant approach were investigated by several workers [20–25], leading to some conclusions about the conditions of applicability of the approach. For example, Chaudhuri [20] treated anharmonic oscillators of the type $(ax^2 + bx^4 + cx^6)$ and showed that, with a particular choice of convergence factor of the form $\exp(-\alpha x^4 + \beta x^6)$, the algebraic of Hill determinant may lead to incorrect eigenvalues; however, Hautot [21], in turn, claimed that the use of this factor with variable β removes this inconsistency (see also [24, 27]).

2.1. *The Double-Well Potential $V(X; Z_x^2, \lambda)$ in One Dimension and the Corresponding Recurrence Relation*

The double-well potential $V_1(x; Z_x^2, \lambda)$ has two minima at $x = \mp x_m \equiv Z/\sqrt{2}\lambda$ and one local maximum at $x = 0$. When Z_x^2 is large, the potential minimum occurs at large value of x, so that the wave function centered at x_m does not penetrate too much through the barrier separating the two wells. The probability of finding the particle is locally maximal at $x = \pm x_m$. Its low energy levels should involve wave functions which present a maximal probability density at a position close to the minimum of the two-well potential. In the case of very deep wells where the tunneling is very small our estimate $|E_{\text{even}} - E_{\text{odd}}|$ for the splitting ΔE is generally too small.

To calculate the energy levels of the Schrödinger equation, we introduce a wavefunction which has the form

$$\Psi_{n_x}(x) = \exp\left(-\frac{\alpha}{2}x^2\right) \sum H(M)(x^{2M}). \tag{8}$$

Substituting this wavefunction into the Schrödinger equation (1) leads to the following four-term difference equation:

$$\begin{aligned}(2M+1)(2M+2)H(M+1) - [4\alpha M + \alpha - E]H(M)\\ + (\alpha^2 + Z_x^2)H(M-1) - \lambda H(M-2) = 0.\end{aligned} \tag{9}$$

We can either take $H(0) = 1$, with all the M's even to get an even solution, or take $H(1)$, with all the M's odd to get an odd solution.

The condition that a nontrivial solution for the $H(M)$ exist is given by the vanishing of the following infinite determinant:

$$D = \begin{vmatrix} E-\alpha & 2 & 0 & 0 & \cdot & \cdot & \cdot & \cdot & \cdot \\ \alpha^2+Z_x^2 & E-5\alpha & 12 & 0 & \cdot & \cdot & \cdot & \cdot & \cdot \\ -\lambda & \alpha^2+Z_x^2 & E-9\alpha & 30 & \cdot & \cdot & \cdot & \cdot & \cdot \\ 0 & -\lambda & \alpha^2+Z_x^2 & E-13\alpha & 56 & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & -\lambda & \alpha^2+Z_x^2 & E-17\alpha & 90 & \cdot & \cdot & \cdot \\ 0 & 0 & 0 & -\lambda & \alpha^2+Z_x^2 & E-21\alpha & 132 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & -\lambda & \alpha^2+Z_x^2 & \cdot & E-4\alpha M-\alpha & 2(M+1)(2M+1) \end{vmatrix}.$$

By using the rules for expanding a determinant and working up the last column, which has only two nonzero elements, we obtain the following recurrence relation for the determinant $D(M)$, obtained by truncating the matrix after $(M + 1)$ rows and columns:

$$\begin{aligned} D(M) = {} & [E - 4\alpha M - \alpha]D(M-1) \\ & + M(M-\tfrac{1}{2})(\alpha^2 + Z_x^2)D(M-2) \\ & - 16\lambda M(M-\tfrac{1}{2})(M-1)(M-\tfrac{3}{2})D(M-3), \end{aligned} \tag{10}$$

where we can use the starting condition $D(-1) = 1$, $D(0) = E - \alpha$, at $M = 1$. $D(1)$, $D(2)$, and so on can then be calculated for any assigned E value. If we use the estimates E_e and $E_2 = E_e + DE$, with DE small, then for each M the values of $D_{E_e}(M)$ and $D_{E_2}(M)$ will give a predicted energy E at which $D_E(M)$ would be zero. We can find several roots for a particular M and we can also follow a particular root as M increases to see whether it tends to limit which is stable to some number of significant figures.

2.2. *The Double-Well Potential in Two-Dimensions and the Recurrence Relation*

The Hill determinant approach is a very powerful technique for calculating eigenvalues in two-dimensional problems. In the present paper we extend the Hill determinant approach to double-well potentials with equal depth Z_x^2 and Z_y^2 (which allows us to deal with the symmetric double-well potential) with its nearly triple degenerate energy levels (E_{00}, E_{11}, E_{10}). We also treat the case of high central barrier and unequal depth Z_x^2 and Z_y^2 (which allows us to deal with the very asymmetric double-well potentials). In order to get a clearer picture, we plot the double-well potential $V_2(x, y; Z_x^2, Z_y^2, \lambda)$ for different values of

Z_x^2, Z_y^2, λ. When Z_x^2 and Z_y^2 are large, the potential minimum occurs at large values of Z_x^2 and Z_y^2, so that the wave function centered at x_m and y_m does not penetrate too much through the central barrier; obviously this is not the case for small values of Z_x^2 and Z_y^2.

To begin our analysis, we take the wavefunction describing this system in the form:

$$\Psi_{nx,ny}(x,y) = \exp\left(-\frac{\alpha}{2}(x^2+y^2)\right] \sum_{M,n} H(M,N)(x^M y^N). \tag{11}$$

The next step is to substitute $\Psi_{nx,ny}(x, y)$ into the Schrödinger equation (1), and after some algebra, we obtain the recurrence relation

$$[2\alpha(M+N+1) - E]H(M,N) = W(M,N), \tag{12}$$

with

$$\begin{aligned} W(M,N) = {} & (M+2)(M+1)H(M+2,N) \\ & + (N+2)(N+1)H(M,N+2) \\ & + (\alpha^2 + Z_x^2)H(M-2,N) \\ & + (\alpha^2 + Z_y^2)H(M,N-2) - \lambda[a_{xx}H(M-4,N) \\ & + 2a_{xy}H(M-2,N-2) + a_{yy}H(M,N-4)], \end{aligned} \tag{13}$$

the recurrence relation (12) is used as follows. First, choose the state numbers n_x and $n_y(0, 1, 2, ...)$ which specify which particular state is being treated. Next take initial values (of M_0 and N_0) to start the calculations, and the coefficient $H(M_0, N_0)$ is set equal to one. All the $H(M, N)$ with $(M, N) \neq (M_0, N_0)$ are then adjusted according to the assignment

$$H(M,N) = W(M,N)[2\alpha(M+N+1) - E]^{-1} \tag{14}$$

for some fixed α and some trial E value, up to finite maximum values of M and N. The energy estimate is then revised using the relation (14) for the special case $M = M_0$, $N = N_0$. The revised energy E_e is

$$E_e = 2\alpha(M_0 + N_0 + 1) - W(M_0, N_0), \tag{15}$$

but it is sometimes useful to set the revised energy equal to

$$E{:} = RE_e + (1 - R)E, \tag{16}$$

where (16) is understood as an assignment statement and R is a relaxation parameter which can be changed in value to help in stabilizing convergence to a desired eigenvalue. After many cycles the energy estimate converges. The upper limits on M and N can then be increased and the calculation repeated, until eventually the energy is not affected by further increase in the upper limits. In matrix-theoretic terms, the calculation is using a Gauss–Seidel ($R = 1$) or successive overrelaxation ($R \neq 1$) approach to calculate the low eigenvalues of a large matrix. Increasing M and N corresponds to increasing the number of basis states, i.e., the dimension of the matrix. In the present approach the relevant matrix elements are very simple, as seen from Eq. (12), and the iterative solution method, although often only useful for low eigenvalues, avoids explicit storage and manipulation of large matrices.

2.3. *The Recurrence Relation for the Double-Well Potential in Three $V(X, Y, Z; Z_x^2, Z_y^2, Z_z^2, \lambda)$ Dimensions*

The algebraic manipulations needed to derive the required recurrence relation in the three dimensions are similar to those which have been used previously in connection with the two-dimensional case. The wavefunction is taken to have the form for three dimensions,

$$\Psi_{n_x,n_y,n_z}(x,y,z) = \exp\left[-\frac{\alpha}{2}(x^2+y^2+z^2)\right] \sum H(M,N,L)(x^M y^N z^L). \tag{17}$$

If we use the wave function $\Psi_{n_x,n_y,n_z}(x, y, z)$ in the Schrödinger equation (1), after some algebra we obtain the following recurrence relations for three dimensions

$$[\alpha(2M+2N+2L+3) - E]H(M,N,L) = W(M,N,L), \tag{18}$$

where

$$\begin{aligned} W(M,N,L) = {} & (M+2)(M+1)H(M+2,N,L) + (N+2)(N+1)H(M,N+2,L) + (L+2)(L+1)H(M,N,L+2) \\ & + (\alpha^2 + Z_x^2)H(M-2,N,L) + (\alpha^2 + Z_y^2)H(M,N-2,L) + (\alpha^2 + Z_z^2)H(M,N,L-2) \\ & -\lambda[a_{xx}H(M-4,N,L) + a_{yy}H(M,N-4,L) + a_{zz}H(M,N,L-4)] \\ & - 2\lambda[a_{xy}H(M-2,N-2,L) + a_{xz}H(M-2,N,L-2) + a_{yz}H(M,N-2,L-2)]. \end{aligned} \tag{19}$$

The strategy for computing the energy eigenvalues in this case is similar to that which has been used to handle the two-dimensional system, so we will only mention the essential features here. The initial condition to start the calculation is that $H(M_0, N_0, L_0) = 1$. All the $H(M, N, L)$ with $(M, N, L) \neq (M_0, N_0, L_0)$ are then calculated sequentially from the relation

$$\begin{aligned} &H(M,N,L) \\ &\quad = W(M,N,L)\,[\alpha(2M + 2N + 2L + 3) - E]^{-1}. \end{aligned} \tag{20}$$

The energy estimate is revised using the relation (20) for the special case $M = M_0$, $N = N_0$, $L = L_0$. The coefficient on the left-hand side becomes $H(M_0, N_0, L_0) = 1$. The revised energy E_e thus takes the form

$$E_e = \alpha(2M_0 + 2N_0 + 2L_0 + 3) - W(M_0, N_0, L_0), \tag{21}$$

but it is sometimes useful to set the revised energy equal to

$$E{:} = RE_e + (1 - R)E. \tag{22}$$

The upper values of M, N, and L can then be increased and the calculation repeated until eventually the energy is unaffected by further increases in the upper limits. The upper limit in our calculation is $(M, N, L = Q = 60)$. The indices have the ranges

$$\begin{aligned} M &= 0, \quad 1, 2, ..., Q \\ (\text{fixed } M) \quad N &= 0, 1, 2, ..., Q \\ (\text{fixed } M, N) \quad L &= 0, 1, 2, ..., Q. \end{aligned}$$

We should point out that Aitken's transformation has been used in order to increase the accuracy of our results and to accelerate the rate of convergence of our calculations.

If S_n, S_{n+1}, S_{n+2} are three successive partial sums, then an improved estimate is

$$S_n = S_n - \frac{[\Delta S_n]^2}{\Delta^2 S_n} = S_n - \frac{[S_{n+1} - S_n]^2}{[S_{n+2} - 2S_{n+1} + S_n]}. \tag{23}$$

The relation (23) has been used to improve the convergence of the calculations and it has helped in improving the accuracy of our listed results in Tables II–IV.

TABLE I

Eigenvalues of Double-Well Potential $V(x; Z_x^2, \lambda)$ in One-Dimensional System for Several Eigenstates E_{n_x}

λ	Z_x^2	n_x	E_{nx}	λ	Z_x^2	n_x	E_{nx}
1.5	2.5	0	0.22045907237212990	0.5	5	0	-9.44697938474047282
		1	2.08829711228774814			1	-9.44562992836759352
		2	5.62389615392606140			2	-3.92153584540274875
		3	9.72354566419132632			3	-3.82087184715860094
		4	14.39139659979008485			4	-0.01344047544363822
		5	19.51362309099289354			5	1.26982440213957438
		6	25.02861634686618382			6	4.03764550800769142
		7	30.89114878246567112			7	6.82884818044587082
		8	37.06704939163747326			8	10.00060195322818555
		9	43.52941805968745698			9	13.41854031318033341
		10	50.25638499717388311			10	17.06745128572262872
1	5	0	-3.41014276123982947	1.5	15	0	-32.12731109560843087
		1	-3.25067536228923598			1	-32.12730965785149255
1	7	0	-8.67110520870420392	5	30	0	-37.42980397877276239
		1	-8.66245222488144421			1	-37.42977455459924215
		2	-2.54370520944282011			2	-23.07960104597809075
		3	-2.11199938221839442			3	-23.07557051062457585
1	10	0	-20.6335767029477978	10	50	0	-52.71004958047889083
		1	-20.6335468844049111			1	-52.71003734557578916
		2	-12.3795437860133029			2	-34.06321714036207558
		3	-12.3756737207056088			3	-34.06136510710378522
		4	- 5.1328379618083858			4	-17.18959999695144949
		5	- 4.9648702736154361			5	-17.08707679490634021
1	25	0	-149.2194561421908880	15	100	0	-152.67831399909375039
		1	-149.2194561421908880			1	-152.67831399908422182
		2	-135.3245120118408585			2	-125.34750268688988602
		3	-135.3245120118408585			3	-125.34750268374595331
		4	-121.6889506046216482			4	-99.06981141974534621
		5	-121.6889506046216482			5	-99.06981095815446581
		6	-108.3280005673323098			6	-73.99094721834865005
		7	-108.3280005673323095			7	-73.99090790696433191
		8	-95.2594596790828367			8	-50.32666184267079224
		9	-95.2594596790827942			9	-50.32455290733653391
		10	-82.5044783545121920			10	-28.47311816811351423
		11	-82.5044783545078108			11	-28.40195685097769502
		12	-70.0887175312348478			12	-9.786565003304405272
		13	-70.0887175308864379			13	-8.499038201171381747
		14	-46.4120052267605372			14	3.909866057170036320
		15	-46.4120041514654285			15	10.487120796491774223
		16	-35.2481845729541083	25	150	0	-207.84995144001516478
		17	-35.2481426274132394			1	-207.84995144001467077
		18	-24.6346811128178588			2	-174.26220711947673746
		19	-24.6334095751947276			3	-174.26220711929462638
		20	-14.7187209354534184			4	-141.82502963460632511
		21	-14.6899524306534688			5	-141.82502960432026387
		22	-5.96094160730292782			6	-110.67561242225776129
		23	-5.53431701894807894			7	-110.67560944362467167
		24	0.66664797113207376			8	-81.00467144058689638
		25	3.12172458243026284			9	-81.00448130057817149
6	40	0	-57.8785897718172453			10	-53.10576879765972895
		1	-57.8785892839732776			11	-53.09769656468204332
		2	-40.9815029067163091			12	-27.59953293185809928
		3	-40.9814099973164893			13	-27.38079541051527492
		4	-25.2783905204222451			14	-6.81834970253106402
		5	-25.2713380978603976			15	-3.93779346508802596
		6	-11.2953528322733256			16	9.55913004229917353
		7	-11.0447433717424087			17	19.22042655903009186

3. RESULTS AND DISCUSSION

The Hill determinant approach has been applied in this paper for double-well potentials in one-, two-, and three-dimensional systems. Eigenvalues for different values of Z_x^2, Z_y^2, Z_z^2, λ and state numbers n_x, n_y, n_z are listed in Tables I–VI. Eigenvalues of such potentials in two- and three-dimensional systems are computed for the first time in this work.

In Table I the values of the energy are calculated over a wide range of $2.5 \leq Z_x^2 \leq 150$ and $0.5 \leq \lambda \leq 25$ for the case of one-dimensional systems, for several eigenstates with even parity and odd parity. It is clear from our listed results in Table I that the Hill determinant approach produces high accuracy despite the large values of λ, Z_x^2, and state number n_x. The computations were carried out to double-precision (20 digits) by using a humus system with Fortran (77) programs.

TABLE II

Eigenvalues of Double-Well Potential $V(x, y; Z_x^2, Z_y^2, \lambda)$ in Two-Dimensional System for Several Eigenstates E_{n_x, n_y}

$a_{xx}=a_{yy}=1, a_{xy}=1$

λ	Z_x^2	Z_y^2	$E_{0,0}$	$E_{1,0}$	$E_{0,1}$	$E_{1,1}$
0.5	0.1	0.2	1.73535914112	4.10168392312	4.02878704179	6.794064109085
1	0.5	1.5	1.61424019660	4.49111439039	3.85624689529	7.298367378617
1.5	1.5	2.5	1.36573363781	4.29273502103	3.69868982791	7.327246077684
2	2.5	3.5	1.10025839746	4.04810630068	3.48052037731	7.243850857804
1	5	6	-4.98397929548	-3.5079641499	-4.76561922859	-2.66915135597
1	10	12	-29.83196949	-27.1296023	-29.831935741	-27.1285681307
1.5	12	15	-30.463174803	-27.14582047	-30.463121839	-27.14442750
1	10	10	-20.69255783668	-20.4574196849	-20.4574196849	-19.76428002530
1	15	15	-50.8775172003	-50.733091622	-50.733091622	-50.3012984043
1	20	20	-93.7526635	-93.647517	-93.647517	-93.33247428
5	1.5	2.5	3.20074097557	8.02716125152	7.67047026747	13.418326341740
10	2.5	4.5	3.91890696042	9.98587120087	9.41475123995	16.655374974567
50	5	7.5	7.49018305786	18.10941723234	17.70649046965	30.242788015342
100	10	15	9.04180811591	22.22034136732	21.57154094623	37.211032187856
200	15	20	11.68043864796	28.32740242124	27.81666229465	47.531226675278
400	30	40	14.01383918430	34.59801844338	33.77421454989	58.304598185255
500	40	50	14.69516952806	36.53932044892	35.76807014538	61.909780228296
10^3	100	120	15.58742224626	41.35189146432	40.06692428309	71.582780162997
10^4	200	250	43.44462308468	104.80661454407	103.42469503214	176.04031655506
10^5	400	500	102.41718804995	239.94712297751	238.70479396810	399.54968738466
10^6	500	750	230.39079493043	533.06550866858	531.64757871875	883.23740723179
10^6	800	10^3	228.57857525990	529.80163820655	528.66379000057	879.01029290318

$a_{xx}=a_{yy}=1, a_{xy}=0$

λ	Z_x^2	Z_y^2	$E_{0,0}$	$E_{1,0}$	$E_{0,1}$	$E_{1,1}$
0.5	0.1	0.2	1.54277696351	3.64852603400	3.57916045652	5.684909527010
1	0.5	1.5	1.28672371395	3.75048552546	3.16648902736	5.630250838881
1.5	1.5	2.5	0.89722227782	3.29180176470	2.76506031773	5.159639804619
2	2.5	3.5	0.48784116273	2.79918890715	2.31413494170	4.625482686126
1	5	6	-9.15833328191	-8.99886588296	-9.11693527841	-8.95746787945
1	10	12	-51.821426429	-51.8213966103	-51.821426079	-51.821396259
1.5	12	15	-51.3617221075	-51.361531115	-51.361720669	-51.36152967
1	7.5	7.5	-20.6748441544	-20.671147346	-20.671147346	-20.66745053753
1	10	10	-41.2671534059	-41.267123587	-41.267123587	-41.2670937688
1	15	15	-101.68277457	-101.68277457	-101.68277457	-101.68277457
5	1.5	2.5	2.71313903038	6.91360663984	6.57975757558	10.780225185045
10	2.5	4.5	3.28728769291	8.54843231401	8.01561749450	13.2767621156
50	5	7.5	6.52382608356	15.87168943395	15.49114157403	24.8390049244
100	10	15	7.76972817142	19.29895353602	18.68900649207	30.2182318566
200	15	20	10.11809317560	24.72775578888	24.24629523816	38.85595785144
400	30	40	11.94612789385	29.88075887479	29.10832025726	47.042951238208
500	40	50	12.40879315446	31.3577635953	30.63677163919	49.5857420801
10^3	100	120	12.22807537841	33.9969073478	32.81963215572	54.5884641251
10^4	200	250	37.74551873112	91.6609991908	90.35696494209	144.272445402
10^5	400	500	91.26949645958	213.7302332201	212.54700375903	335.007740519
10^6	500	750	207.51880809728	478.7462390699	477.39009393699	748.617524909
10^6	800	10^3	205.49861617278	475.0983276177	474.01087832324	743.610589768

In order to illustrate the effect of increases of the state number n_x on degeneracy of energy levels at given values of λ and Z_x^2, we calculated many eigenvalues. For example, at $\lambda = 1$ and $Z_x^2 = 25$, 26 energy levels are calculated. It is clear that as n_x increases the splitting $|E_{\text{even}} - E_{\text{odd}}| = \Delta E$ increases also.

Some important consequences have come from our investigations for double-well potentials in one-dimensional systems: If Z_x^2 increases, the energy levels for states of even and odd parities become effectively degenerate, i.e., $E_{\text{even}} = E_{\text{odd}}$, for instance; the corresponding energies of these states at $Z^2 = 25$, $\lambda = 1$ are $E_0 = E_1 = -149.219456142190880$. Similar considerations hold for other higher values of Z_x^2, as is clear from listed results in Table I and this confirmed the results conjectured by the works [1–11] for the case of double-well potentials in one-dimensional systems.

In Table II the values of the energy are calculated over a wide range of $0.1 \le Z_x^2, Z_y^2 \le 10^3$, and $0.5 \le \lambda \le 10^6$ for the double-well potential $V_2(x, y; Z_x^2, Z_y^2, \lambda)$ in two dimensions for two cases $a_{xx} = a_{yy} = a_{xy} = 1$ and $a_{xx} = a_{yy} = 1$, $a_{xy} = 0$ for four eigenstates E_{00}, E_{11}, E_{10}, and E_{01}.

When the potential $V_2(x, y; Z_x^2, Z_y^2, \lambda)$ is separable, i.e., $a_{xy} = 0$, the total energy $E_{nx,ny}$ of a state is the sum of two components $E_t = E_x + E_y$. But when $a_{xy} \neq 0$ the potential is nonseparable and the total energy of a state is the sum of the three components $E_t = E_x + E_y + E_{xy}$. When the system is separable it is clear that the splitting ΔE vanishes for higher values of Z_x^2, Z_y^2, in contrast to the nonseparable system, and this is clear from our listed results.

As a general remark, we note the degree of accuracy (i.e., the number of digits) in the eigenvalues that we have been able to obtain by our approach appears to diminish slowly with the increase in the values of Z_x^2, Z_y^2 at the given values of λ. Also the accuracy possible is usually greater for larger values of λ than for smaller values of λ, at the same values of Z_x^2, Z_y^2.

It is interesting to note that the energy levels characterized by (n_x, n_y) with n_x and n_y having different parity, i.e., odd–even or even–odd, remain doubly degenerate and unsplit when the double well potential has exchange symmetry but for the unsymmetrical case the double energy level splits into two different separate levels. The energy levels showing such behaviour are E_{01} and E_{10}, and this is clear from the listed results in Table II.

Accurate eigenvalues were obtained in all ranges of perturbation parameters for the potential $V_2(x, y; Z_x^2, Z_y^2, \lambda)$. The results agreed with those (when available) from other works [1–11]. For the special case $Z_x^2 = Z_y^2 = Z^2$, $a_{xx} = a_{yy} = 1$, $a_{xy} = 0$, the potential (3) reduces to the two independent double-well potentials.

The energy eigenvalues for the three-dimensional system $V_3(x, y, z; Z_x^2, Z_y^2, Z_z^2, \lambda)$ are calculated, and their energy eigenvalues are quoted in Table IV, for several eigenstates and various values of Z_x^2, Z_y^2, Z_z^2 and λ.

In Tables III and IV emphasis is specially placed on the larger values for the case $Z_x^2 = Z_y^2 = Z_z^2 = Z^2$ because the eigenvalues for different states E_{000}, E_{100}, E_{010}, E_{011}, E_{110}, E_{101}, E_{111} have almost degenerate eigenvalues. As Z^2 increases, the magnitude of the splitting between these levels decreases, i.e., $|E_{111} - E_{000}| = |E_{110} - E_{100}| = \Delta E \cong 0$, as is clear from listed results in Tables III and IV and this confirmed the results conjectured by the works [1–11] for the case of the double-well potential in one dimension.

When the potential $V_3(x, y, z; Z_x^2, Z_y^2, Z_z^2, \lambda)$ is separable, i.e., $a_{xy} = a_{xz} = a_{yz} = 0$, the total energy $E_{nx,ny,nx}$ of a state is the sum of three components $E_t = E_x + E_y + E_z$. But when $a_{xy} = a_{xz} = a_{yz} \neq 0$ the potential is nonseparable and the total energy of a state is the sum of six components $E_t = E_x + E_y + E_z + E_{xy} + E_{xz} + E_{yz}$. When the system is separable, it is clear that the splitting ΔE vanishes for higher values of Z_x^2, Z_y^2, Z_z^2, in contrast to nonseparable system, and this clear from our listed results.

It should be pointed out that the energy levels characterized by eigenstates Ψ_{100}, Ψ_{010}, Ψ_{001} and Ψ_{110}, Ψ_{011}, Ψ_{101} remain triply degenerate and unsplit for the double-well potential with symmetrical behaviour as λ is varied from the value of zero. This means that the perturbation does not break the degeneracy of the perturbed system, but for the case of unsymmetrical double-well potentials the triplet degenerate levels split into three, and this is confirmed by our results in Tables III and IV.

We have plotted the variation of the first few energy levels in Figs. 3–6 as function of Z^2 to display the degeneracy of energy levels for our results in the Tables II–IV for the double well potential in two- and three-dimensional systems for the symmetrical case of the energy levels E_{00}, E_{10}, E_{11} and E_{000}, E_{100}, E_{110}, E_{111} for different values of

TABLE III

Eigenvalues of Double-Well Potential $V(x, y, z; Z_x^2, Z_y^2, Z_z^2, \lambda)$ in Three-Dimensional System for Several Eigenstates E_{n_x,n_y,n_z}, for the Case $a_{xx} = a_{yy} = a_{zz} = a_{xy} = a_{xz} = a_{yz} = 1$

λ	Z_x^2	Z_y^2	Z_z^2	$E_{0,0,0}$	$E_{1,0,0}$	$E_{0,1,0}$	$E_{0,0,1}$
0.5	0.1	0.2	0.3	2.7827992267501	5.3685338354291	5.29982177526	5.22975043061
0.5	0	0.4	0	2.770318719513	5.42713073659	5.00216309799	5.42713073659
1.5	0.5	1.5	2	3.19734167311	6.89575498784	6.39486141405	6.12378760059
1	0	2	0	2.56531234696	6.08182958128	4.16036840171	6.08182958127
1	2	4	6	-2.67383926	0.92990283	-0.34274002784	-2.4253434496
1	0	5	0	-1.08165433232	3.501975779	-0.9411507857	3.501975783
1	15	15	15	-50.84138728	-50.55290971	-50.55290971	-50.55290971
1	20	20	20	-93.7263709	-93.5161789	-93.5161789	-93.5161789
50	4	8	16	11.55954962921	23.464392285554	22.86231111487	21.5859637258
10^2	5	10	15	15.6197857129	30.63723857	30.04363488	29.43235907
10^3	20	40	60	34.27260600974	66.72376925785	65.62665610429	64.501750817
10^4	50	75	100	78.6868350736	149.09208894	148.46513705	147.83410874
10^5	100	200	300	172.4521647994	325.32572406	324.169159946	323.00619023
10^6	250	500	10^3	374.68114631674	704.82321601527	703.4853626709	700.797750693
10^2	500	10^3	10^4	342.87770738580	675.68133437335	673.0127649054	622.016518347

λ	Z_x^2	Z_y^2	Z_z^2	$E_{0,1,1}$	$E_{1,0,1}$	$E_{1,1,0}$	$E_{1,1,1}$
0.5	0.1	0.2	0.3	8.1048349028977	8.1674025449811	8.231227813162	11.3207903727
0.5	0	0.4	0	8.023566759879	8.410685440812	8.023566759879	11.3045532269
1.5	0.5	1.5	2	9.92052973264	10.37018913604	10.61393631032	14.5724836294
1	0	2	0	8.20915289337	9.94053727485	8.20915289337	12.5153832032
1	2	4	6	0.4239965828	1.527046205	3.351486825	4.55341104
1	15	15	15	-49.97887929	-49.97887929	-49.97887929	-49.12482824
1	20	20	20	-93.0965841	-93.0965841	-93.0965841	-92.4691335
50	4	8	16	34.68230678074	35.2265013113	36.381373687	49.59461199
10^2	5	10	15	46.009176836	46.5482042643	47.103550794	64.7586425039
10^3	20	40	60	100.4380473191	101.4355073920	102.458655448	140.88591552
10^4	50	75	100	227.024464662	227.596990012	228.17329389	314.33293385
10^5	100	200	300	494.80143445	495.85885273	496.92221416	683.81397538
10^6	250	500	10^3	1072.6030895918	1073.8269796306	1076.285808337	1480.34788565
10^6	500	10^3	10^4	998.5727443477	1000.9984377559	1047.399135135	1410.53324073

TABLE IV

Eigenvalues of Double-Well Potential $V(x,\ y,\ z;\ Z_x^2, Z_y^2, Z_z^2, \lambda)$ in Three-Dimensional System for Several Eigenstates E_{n_x,n_y,n_z}, for the Case $a_{xx} = a_{yy} = a_{zz} = 1$, $a_{xy} = a_{xz} = a_{yz} = 0$

λ	Z_x^2	Z_y^2	Z_y^2	$E_{0,0,0}$	$E_{1,0,0}$	$E_{0,1,0}$	$E_{0,0,1}$
0.5	0.1	0.2	0.3	2.2408571315938	4.346606202039	4.277240625013	4.20695421379
1.5	0.5	1.5	2.5	1.94680237642	4.843006792815	4.341381883032	3.81464045247
1.5	4	5	6	-5.40488058	-4.327837	-4.783406	-5.107749
2	6	8	10	-14.458991387	-13.7541496574	-14.267608029	-14.42566512
1	15	15	15	-152.524161853	-152.524161852	-152.524161852	-152.52416185
1	20	20	20	-281.179112753	-281.179112753	-281.179112753	-281.17911275
10^2	5	10	15	12.2925753312	24.42032606563	23.821800689	23.21185364
10^3	20	40	60	27.2569441109	53.56167945482	52.454864648	51.329698146
10^4	0	75	100	65.53822945738	124.55489455	122.66355744	122.0273496
10^4	50	75	100	64.6892793	122.4479325	121.8146075	121.1783997
10^5	0	200	300	143.7074491	270.8549997	268.5208068	267.3468018
10^5	100	150	300	143.3201497	269.3029046	268.7187815	266.9595023
10^6	0	500	10^3	312.6345561	586.565650	583.8619873	581.1468185
10^6	0	10^3	10^4	274.1824538977	548.113547	542.694715	491.87077366
10^6	750	900	10^3	308.43201727621	578.30330304805	577.4882343745	576.944279558

λ	Z_x^2	Z_y^2	Z_y^2	$E_{0,1,1}$	$E_{1,0,1}$	$E_{1,1,0}$	$E_{1,1,1}$
0.5	0.1	0.2	0.3	6.243337707534	6.312703284864	6.38298969406	8.34908677541
1.5	0.5	1.5	2.5	6.20921995312	6.71084486935	7.23758629991	9.10542436999
1.5	4	5	6	-4.4862778	-4.0307065	-4.4862778	-3.409234418
2	6	8	10	-14.234289	-13.720828	-13.56276628	-13.5294444
1	15	15	15	-152.52416185	-152.52416185	-152.52416185	-152.52416185
1	20	20	20	-281.17911275	-281.17911275	-281.17911275	-281.17911275
10^2	5	10	15	34.741079028	35.3396044	35.949551	46.8688297
10^3	20	40	60	76.527618654	77.6344334656	78.7595999584	102.83235398
10^4	0	75	100	179.1526779	181.044014	181.680222	238.169342
10^4	50	75	100	178.3037278	178.9370528	179.5732606	236.0623809
10^5	0	200	300	392.160159	394.4943523	395.668356	519.3077099
10^5	100	150	300	143.3201497	392.9422581	394.7015372	518.3408903
10^6	0	500	10^3	852.3742497	855.0779127	857.7930815	1126.3053438
10^6	750	900	10^3	846.00049660573	846.8155652763	847.3595201926	1115.87178229
10^6	0	10^3	10^4	760.383035959	765.8018675503	816.6258098755	1034.31412965

Z^2. We can observe in Figs. 3–6 that the energy levels are degenerate for higher values of Z^2.

It is important to point out that the adjustable parameter α has played an important role in the convergence of our calculations. The best α values in this calculation have been obtained by numerical search, so our calculation reveals the importance of finding the best values of the adjustable parameter α. The general consideration governing our choice is that, as λ increases, the value of α increases. Table VI compares some samples of the convergence of our results for various values of an adjustable parameter α for the states Ψ_{111} and Ψ_{000}.

When $Z_x^2 = Z_y^2 = Z_z^2 = Z^2$ and for large values of Z^2 with small values of λ, the convergence rate of our algorithm for the calculation of energy levels is improved if we applied the scaling $(x_I \rightarrow a x_I)$ to the Schrödinger equation

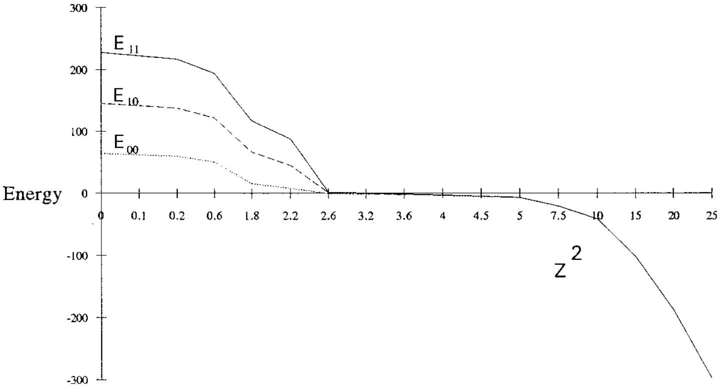

FIG. 3. Graph of three energy levels $E_{nx,ny}$ for the potential $V_2(x, y; Z_x^2, Z_y^2, \lambda = 1)$ for different values of Z^2 ($Z_x^2 = Z_y^2 = Z^2$) for the case $a_{xx} = a_{yy} = 1$, $a_{xy} = 0$. For small values of Z^2, the positive energies are small; then it is necessary to multiply these energies by a factor of 30 in order to obtain a clear figure.

TABLE V

Comparison of Some Eigenvalues Which Have Been Calculated by the Hill Determinant Approach with Those Corresponding Calculations Available in the Literature for One- and Three-Dimensional Systems

Z_x^2	λ	n_x	E_{n_x}	Other works & Ref.[no.]	
1	1	0	0.65765300518071512305	0.657653005180715	[7]
		1	2.83453620211930421465	2.834536202119305	
15	1	0	-50.84138728438195436625	-50.8413872844	[3]
		1	-50.84138728418700515471	-50.8413872842	
50	1	0	-615.02009090275781656621	-615.02009090275781656622	[5]
		1	-615.02009090275781656501	-615.02009090275781656501	

$Z_x^2=Z_y^2=Z_z^2=Z^2$, $a_{xx}=a_{yy}=a_{zz}=1; a_{xy}=a_{xz}=a_{yz}=0$

Z^2	λ	n_x	n_y	n_z	E_{n_x,n_y,n_z}	Other Works& Ref.	[no]
0.5	1	0	0	0	2.6100525551148	2.610052555114836	[4]
		1	0	0	5.0738143666302	5.073814366630231	
		1	1	0	7.5375761781456	7.537576178145625	
		1	1	1	10.0013379896622	10.001337989661019	
5	1	0	0	0	-10.230428283777	-10.23042828371949	[5]
		1	0	0	-10.070960884548	-10.07096088476889	
		1	1	0	-9.911493485618	-9.91149348581830	
		1	1	1	-9.752026086957	-9.75202608686771	
10	1	0	0	0	-61.90073010	-61.90073010884310	[7]
		1	0	0	-61.9007003	-61.90070029029515	
		1	1	0	-61.9006704	-61.90067047174719	
		1	1	1	-61.9006406	-61.90064065319925	

(2) it follows that the potentials take the following form:

in one dimension,

$$V_1(x;\beta) = -x^2 + \beta x^4; \tag{24}$$

in two dimensions,

$$V_2(x, y;\beta) = -(x^2 + y^2) + \beta[a_{xx}x^4 + 2a_{xy}x^2y^2 + a_{yy}y^4]; \tag{25}$$

and in three dimensions,

$$\begin{aligned} V_3(x, y, z;\beta) = -(x^2 + y^2 + z^2) + \beta[a_{xx}x^4 + a_{yy}y^4 \\ + a_{zz}z^4 + 2a_{xy}x^2y^2 + 2a_{xz}x^2z^2 + 2a_{yz}y^2z^2], \end{aligned} \tag{26}$$

where $\beta = Z^{-3}\lambda$ and the energy $E(Z^2, \lambda) = ZE(1, \beta)$.

Comparison with the results of other methods has been made in Table V for the double-well potential in one and three dimensions, for various values of Z^2, λ, and several sets of eigenfunctions. The first comparison was made with numerical results for the one dimensional system. It is clear from Table IV that there is agreement between our results and the previously published results of Balsa *et al.* [3], Hodgson and Varshni [5], and Saavedra and Buendia [7] up to 12, 21, 16 decimal places, respectively. The second comparison, in three dimensions is for the case a_{xx} =

TABLE VI

Convergence for Some Eigenvalues for $E_{nx,ny,nz}$ of Double-Well Potential $V(x, y, z; Z_x^2, Z_y^2, Z_z^2, \lambda)$ for the Case $a_{xx} = a_{yy} = a_{zz} = a_{xy} = a_{xz} = a_{yz} = 1$ for Several Sets of Parameters Z_x^2, Z_y^2, Z_z^2, and λ, for Various Values of Adjustable Parameter α.

λ	Z_x^2	Z_y^2	Z_z^2	E_{000}	E_{111}	α
1	1	1.5	2			2
				2.2748	11.64	3
				2.2748608046922	11.647929865569	4
				2.2748608046	11.647929866	6
10	1	2	3			5
				7.3196074892564	30.211321634816	10
				7.3196074	30.211322	15
				7.32	30.21	20
10^3	50	75	100			20
				30.84701	133.38	30
				30.847015696039	133.38383535060	40
				30.8470156960	133.383835350	50
10^6	400	500	600			200
				375.	1482.	260
				375.44434786	1482.07203	360
				375.44434786480	1482.0720390537	420
				375.44434786	1482.07203905	460

Note. The empty spaces mean the eigenvalues cannot be obtained with these values of α.

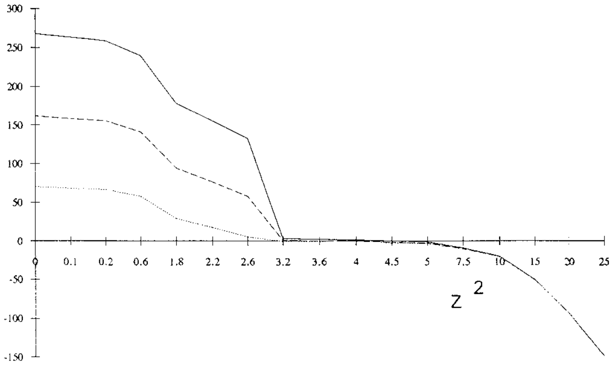

FIG. 4. Graph of three energy levels $E_{nx,ny}$ for the potential $V_2(x, y; Z_x^2, Z_y^2, \lambda = 1)$ for different values of Z^2 ($Z_x^2 = Z_y^2 = Z^2$) for the case $a_{xx} = a_{yy} = 1$, $a_{xy} = 1$. For small values of Z^2, the positive energies are small; then it is necessary to multiply these energies by a factor of 30, in order to obtain a clear figure.

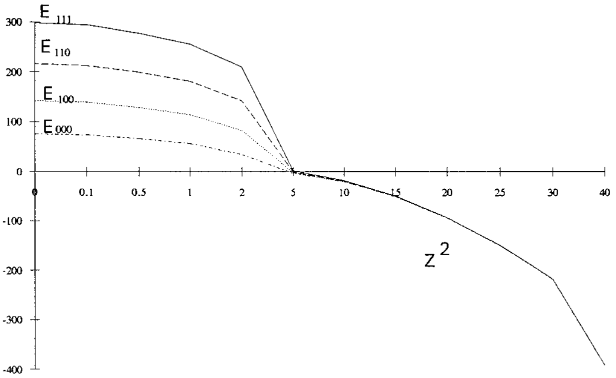

FIG. 5. Graph of four energy levels $E_{nx,ny,nz}$ for the potential $V_3(x, y, z; Z_x^2, Z_y^2, Z_z^2, \lambda = 1)$ for different values of Z^2 ($Z_x^2 = Z_y^2 = Z_z^2 \equiv Z^2$) for the case $a_{xx} = a_{yy} = a_{zz} = 1$, $a_{xy} = a_{xz} = a_{yz} = 1$. For small values of Z^2, the positive energies are small; then it is necessary to multiply the energies by a factor of 20, in order to obtain a clear figure.

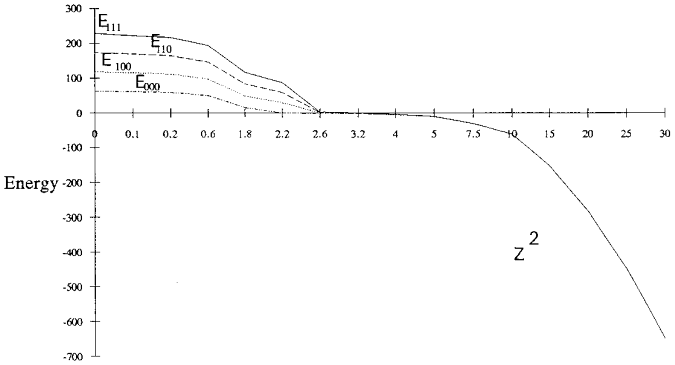

FIG. 6. Graph of four energy levels $E_{nx,ny,nz}$ for the potential $V_3(x, y, z; Z_x^2, Z_y^2, Z_z^2, \lambda = 1)$ for different values of Z^2 $(Z_x^2 = Z_y^2 = Z_z^2 \equiv Z^2)$ for the case $a_{xx} = a_{yy} = a_{zz} = 1$, $a_{xy} = a_{xz} = a_{yz} = 0$. For small values of Z^2, the positive energies are small; then it is necessary to multiply the energies by a factor of 20, in order to obtain a clear figure.

$a_{yy} = a_{zz} = 1$, $a_{xy} = a_{xz} = a_{yz} = 0$; with other workers results [4, 5, 7]. At higher values of $Z^2 = 10$, at $\lambda = 1$, it was found that the Hill determinant approach faced greater convergence difficulties in the three-dimensional case. Such comparison shows that the present technique is highly accurate. Higher accuracies still can be achieved at the expense of greater computation times.

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