

Perturbative-variational calculations in two-well anharmonic oscillators

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The perturbative-variational method is used with a nonorthogonal basis set whose elements are combinations of two harmonic-oscillator functions symmetrically shifted around the origin in order to approximate the eigenvalues and eigenfunctions of the two-well anharmonic-oscillator potential [$V(x) = -Z^2x^2 + x^4$ with $Z^2 > 0$]. This basis set is rather adequate for this potential and allows one to calculate not only the ground-state energy but also the energy of the excited states with very high precision.

I. INTRODUCTION

The practical application of nondegenerate perturbation theory to the approximation of the eigenvalues and eigenfunctions of the one-dimensional Schrödinger equation has always been difficult to accomplish if we try to achieve high precision. The main reasons are the slow convergence of the perturbative results, the asymptotic character of the expansion in some cases, and, for the quartic anharmonic oscillator, the nonconvergence of the expansion.¹ The inclusion of one or more free parameters in the auxiliary basis set in which we perform the perturbative expansion corrects for these deficiencies, by controlling and accelerating the convergence of the expansions not only for the eigenvalues, but also for the eigenvectors,^{2,3} and high-precision results are attained for several kinds of potentials.^{4,5}

Although this procedure can be applied to any kind of potential, it must be pointed that there are strong restrictions for its practical application. The origin of these restrictions is the high order of the perturbation series, which are necessary if high precision is required. This results in the disposal of some algorithms that allow a fast and accurate calculation of the expectation values that appear in the perturbation series. Therefore the use of perturbation theory has been reduced to potentials and basis sets that allow an analytical calculation of their expectation values; i.e., in previous works, the harmonic-oscillator basis set and polynomial^{2,3} or a ratio of polynomial potentials have been used.^{5,6} It is obvious that in this case the choice of adequate free parameters is rather limited, and only the strength of the harmonic oscillator has been used in this sense. This restriction is especially important for some potentials, such as the two-well anharmonic oscillator [$V(x) = -Z^2x^2 + x^4$ with $Z^2 > 0$]. The double-well structure of this potential causes its eigenfunctions to be approximated badly by harmonic-oscillator functions centered in $x = 0$ for values of $Z^2 > 5$, when the depth of the wells is important.

For this potential, the natural choice for an auxiliary basis set of functions is a sum of two harmonic-oscillator functions symmetrically shifted from the origin of the coordinates. With this basis set, the shifted distance may

be incorporated as another free parameter that can be added to the strength of the oscillator. The nonorthogonality of this set basically has limited its use. However, within the perturbative-variational approximation the nonorthogonality does not impose a limitation to the method. Our aim is to show that the main limitation of this kind of procedure is the calculation of the matrix elements that appear in the perturbation series and that the nonorthogonality of the basis only implies the additional calculation of the overlaps between the basis functions.

We have not yet discussed the criteria that can be used to fix the free parameters that appear in the auxiliary basis set; for the case mentioned above, there are two: the oscillator strength and the displacement from the origin of the oscillator functions. The most widely used criterion,^{2,6,7} with N , the maximum order of perturbation, fixed, is to impose that the perturbative estimate of the eigenvalue in this order is stationary with respect to the variation of the free parameters. This may be considered the most natural form within the perturbation scheme. Another similar criterion, although it is not equivalent to the first one, is to make the norm of the N -order perturbation contribution to the eigenfunction stationary. A different and very interesting criterion consists in taking the approximations to the successive perturbative orders as a family of trial wave functions and then applying the Rayleigh-Ritz variational criterion. We will call this working within the perturbative-variational approximation. This last criterion has been recently studied⁸ for the quartic anharmonic oscillator, and a close parallelism has been seen with the perturbative criterion with respect to the norm of the wave function. We must mention that, although the variational method provides strict upper bounds only for the ground state, the high precision of the calculations given by the perturbative-variational method allows one to apply it with similar effectiveness to the excited states. The loss of precision is only important for highly excited states.

Here we shall try to apply the perturbative-variational approximation to the two-well anharmonic oscillator with a nonorthogonal auxiliary basis set. We shall first review the perturbation method for the nonorthogonal basis set. After this, we shall describe the basis that we

shall used in our study. We shall discuss the obtained results, and finally, we shall comment on the conclusions.

II. DESCRIPTION OF THE METHOD

We shall represent our nonorthogonal basis set for $\{|\Phi_k\rangle\}_{k=0}^{\infty}$, where we have introduced one or more free parameters that, by now, are not necessary to write in an explicit way. Let H be our problem Hamiltonian, and let us write $|\psi_n\rangle$ and E_n for the eigenvectors and eigenvalues of the corresponding eigenvalue equation:

$$H|\psi_n\rangle = E_n|\psi_n\rangle. \quad (1)$$

The approximation of these eigenvalues and eigenfunctions is the proposal of our study.

In order to generate the perturbative approximation, we shall expand the exact eigenfunctions in terms of the vectors of our nonorthogonal basis:

$$|\psi_n\rangle = \sum_{k=0}^{\infty} C_{n,k} |\Phi_k\rangle. \quad (2)$$

After this, we substitute (2) in the eigenvalue equation (1) and project over the state $|\Phi_m\rangle$. When we do this, we obtain a set of equations for the coefficients $C_{n,k}$:

$$\sum_{k=0}^{\infty} C_{n,k} (H_{mk} - E_n A_{mk}) = 0, \quad m=0,1,\dots, \quad (3)$$

where $H_{mk} = \langle \Phi_m | H | \Phi_k \rangle$ and $A_{mk} = \langle \Phi_m | \Phi_k \rangle$ is the overlap matrix. At this point, we have not made any kind of approximation and the corresponding solutions involve a generalized eigenvalue problem. This can be drastically simplified using the *perturbation approximation*. As the first approximation for the n th level, all the coefficients in (2) will be zero unless they correspond to $k=n$, and they will be equal to 1, that is, $C_{n,k}^{(1)} = \delta_{nk}$, with the superindex (1) meaning the approximation of first order. This leads to $E_n^{(1)} = H_{nn} / A_{nn}$ as the perturbative approximation of first order for the eigenvalue E_n . The approximations for the successive orders are obtained by applying (3), keeping the condition $C_{nn}^{(l)} = 1$ for every l . Thus we can obtain the coefficients corresponding to the $(l+1)$ th order in a recursive way from the coefficients of the l th order. Explicitly,

$$C_{n,m}^{(l+1)} = \frac{\sum_{k(l) \neq m(l)} (H_{mk} C_{m,k}^{(l)} - A_{mk} E_n^{(l)})}{A_{mm} E_n^{(l)} - H_{mm}}, \quad m \neq n \quad (4)$$

$$E_n^{(l+1)} = \frac{\sum_{k=0}^{\infty} C_{n,k}^{(l+1)} H_{nk}}{\sum_{k=0}^{\infty} C_{n,k}^{(l+1)} A_{nk}}. \quad (5)$$

These formulas are the starting point of the Brillouin-Wigner perturbation formula.⁹ It is important to note the role of the perturbation approximation that transforms a generalized eigenvalue problem in a simple recursive problem and that the structure of the coefficients is completely determined by the perturbative hypothesis.

The validity of the perturbation approximation for a particular problem depends essentially on how well the vector of the basis set to which we shall apply the perturbation approximates the exact eigenfunction. We try to satisfy this basic requirement by introducing free parameters in the functions and by using an appropriate fitting of the elements of the basis to our problem.

In general, we must note that for any Hamiltonian, and even for the second order perturbation approximation, all the coefficients in the expansion of the eigenvectors are nonzero. However, if the basis set is suitably chosen and its free parameters are fixed with their optimal values, the absolute values of the coefficients will decrease quickly around the coefficient $k=n$, which is equal to 1 for every order. This behavior ensures that the necessary cut in the number of the states of the basis set when we perform a practical calculation will not affect the precision in the results. Obviously, this cut must be done for a state with $k_{\max} \gg n$. Keeping this practical restriction in mind, we can write the l th-order perturbation approximation for the exact eigenvalue n as

$$|\Psi_n^{(l)}\rangle = \sum_{k=0}^{k_{\max}} C_{n,k}^{(l)} |\Phi_k\rangle, \quad l=1,2,\dots \quad (6)$$

Note that $C_{n,k}^{(l)}$ and $|\Phi_k\rangle$ depend on free parameters. Therefore, $|\Psi_n^{(l)}\rangle$ for any order l can be seen as a set of trial wave functions, and we can use the variational criterion in order to fix the free parameters. In this way, we have used the perturbation approximation for generating trial wave functions for the variational method. The variational criterion ensures that the expectation values of our Hamiltonian between any of the functions $|\Psi_n^{(l)}\rangle$ are upper bounds to the ground-state energy. However, as we shall see, the eigenvalues of the excited states are approximated with high precision when we use the corresponding value of n and for perturbation orders in which we obtain stability.

It is very important to point out that in many cases the direct iterative process for generating the successive perturbative approximations, shown in Eqs. (4) and (5), is not stable and leads to bad results. A procedure that does not have this kind of problems and that increases the speed of the convergence is the Gauss-Seidel method,¹⁰ which uses the coefficients that we have calculated in the $l+1$ iteration to obtain the coefficients in the same iteration for a larger m . That is, we replace Eq. (4) for

$$C_{n,m}^{(l+1)} = \frac{\sum_{k(<m)} [H_{mk} C_{m,k}^{(l+1)} - A_{mk} E_n^{(l)}] + \sum_{k(>m)} [H_{mk} C_{m,k}^{(l)} - A_{mk} E_n^{(l)}]}{A_{mm} E_n^{(l)} - H_{mm}}. \quad (7)$$

In a certain sense, the Gauss-Seidel method breaks down the basic structure of the perturbation theory, because it mixes the orders l and $l+1$ for determining the order $l+1$, but it must be noted that in the zone where the perturbative corrections are small, Eqs. (4) and (7) are almost equivalent and the functions associated with these coefficients are the best variational estimators as we shall see in the cases that we shall analyze now.

III. TWO-WELL ANHARMONIC OSCILLATOR

There is no doubt that the two-well anharmonic oscillator is an optimal example for the application of the proposed method. On the one hand, its Hamiltonian in the coordinate representation can be written as

$$H = -\frac{d^2}{dx^2} - Z^2x^2 + x^4. \quad (8)$$

It has a quite simple structure, and if the vectors of the basis set are simple combinations of oscillator functions, the matrix elements required by the approximation can be calculated analytically. On the other hand, the structure of the double well for any value of Z^2 , i.e., different depth, allows one to think that a first reasonable approximation for the different eigenstates will be a combination of two oscillator functions with the same number of quanta centered around the two minima of the potential, shifted to the right and left a distance a approximately equal to the position of the minima.

This set of functions is adequate to be used as a nonorthogonal basis in which we can expand the perturbative-variational trial wave functions $|\Psi_n^{(l)}\rangle$. That is, we shall work with the set of nonorthogonal basis defined as

$$\Phi_n^{(+)}(x; a, \alpha) = \phi_n(\alpha(x+a)) + (-1)^n \phi_n(\alpha(x-a)), \quad n=0, 1, \dots \quad (9)$$

$$\Phi_n^{(-)}(x; a, \alpha) = \phi_n(\alpha(x+a)) - (-1)^n \phi_n(\alpha(x-a)), \quad n=0, 1, \dots \quad (10)$$

where $\phi_n(\alpha z)$ is the harmonic-oscillator function corresponding to the n th level:

$$\phi_n(\alpha z) = \left[\frac{\alpha}{\sqrt{\pi} 2^n n!} \right]^{1/2} H_n(\alpha z) \exp \left[-\frac{(\alpha z)^2}{2} \right]. \quad (11)$$

H_n is the Hermite polynomial of order n . The superscripts (+) and (-) are the corresponding parity of the basis functions. This nonorthogonal set $\{\Phi_n^{(+)}, \Phi_n^{(-)}\}_{n=0}^{\infty}$ obviously form a nonorthogonal basis of the set of all square integrable functions on the real line ($L^2[\mathbb{R}]$).

We have chosen our basis set of functions with well-defined parity, because the Hamiltonian associated with the two-well anharmonic oscillator (8) commutes with the parity. This implies that when we construct the functions $|\Psi_n^{(l)}\rangle$ for the different orders, taking as initial function one of the $|\Phi_n^{(\pi)}\rangle$ ($\pi = +, -$), both states will have the same parity. This will allow us to write $|\Psi_n^{(l)}\rangle^{(+)}$ or

$|\Psi_n^{(l)}\rangle^{(-)}$, depending on whether we have initially used $|\Phi_n^{(+)}\rangle$ or $|\Phi_n^{(-)}\rangle$, respectively. The different eigenvalues of the problem Hamiltonian are approximated by the expectation values of this Hamiltonian. Therefore we must note that in the corresponding perturbative-variational states $|\Psi_n^{(l)}\rangle^{(\pi)}$, strict upper bounds will be obtained not only for the ground state, but also for the first excited state, because they have opposite parity and are mutually orthogonal. Obviously, as we have already mentioned in the Introduction, for the rest of the excited states $|\Psi_n^{(l)}\rangle^{(\pi)}$, $n \neq 0$, the variational method does not provide upper bounds to the corresponding eigenvalues. However, the characteristic of the method allows that, for sufficiently large values of (l) that make the coefficients stable in (6), the functions obtained are almost orthogonal to the lower-energy states, and the estimations of the energy are excellent approximations to the exact eigenvalues. Since there is a difference of the results provided by the method for the ground state (and the first excited state) and the rest of the excited states, we provide separate discussions for these cases.

IV. GROUND AND FIRST EXCITED STATES

The minimum upper bounds obtained for these first two states for different values of Z^2 are shown in Table I. In all cases, we have used the Gauss-Seidel method. The corresponding number in the k_{\max} column is the minimum number of states of the basis set necessary for obtaining stable results; i.e., if we use a value greater than k_{\max} , we get the same result, but if we use a value smaller than k_{\max} , although there is stability, the value of the bound is higher than the one obtained in the other cases. In all the cases shown in Table I, our results coincide with the ones of Balsa *et al.*¹¹ who use a high-precision technique, based on the solution of the Hill determinant, with a harmonic-oscillator basis with free strength. It is also very interesting to compare the results of Fernandez, Meson, and Castro,⁶ who use the perturbation approximation with a standard harmonic oscillator basis set with free strength. They fix this parameter using the first criterion mentioned in the Introduction. Our results coincide with theirs, although it must be noted that they need a higher perturbation order to obtain stability for $1 < Z^2 < 10$. Also, they cannot calculate for $Z^2 > 10$ because there are serious problems of stability. This last fact justifies the use of this nonorthogonal basis for this problem.

In the practical application of the method proposed here for these states and for the rest of the excited states, it must be emphasized that for a wide range of values of the variational parameters a and α the method converges quickly and to the same expectation value, although the perturbation order needed to obtain stability depends on the values of the free parameters. For example, for $Z^2=1$ and working with $a=0$, $\alpha=1.58$, and in order 16, we get a similar result to the one shown in Table I. This behavior allows us to use for the calculation the values of the free parameters α and a that minimize the energy when we use the unperturbed function corresponding to $l=1$ (i.e., the values that minimize $E_m^{(1)}$). We have

TABLE I. Ground- and the first-excited-state energies (in units $\hbar/2m = 1$) for different values of Z^2 . The values of the variational parameters α and a are also given. N is the order of the perturbation expansion with which we obtain convergence, and k_{\max} is the number of the maximum states of the basis set used in the calculation. The parity of state is given by p .

Z^2	α	a	N	p	E	k_{\max}
0	1.20	0.00	30	+	1.060 362 090 484 183	50
				-	3.799 673 029 801 394	
1	1.54	0.58	11	+	0.657 653 005 180 715	60
				-	2.834 536 202 119 305	
5	1.81	1.42	19	+	-3.410 142 761 239 826	100
				-	-3.250 675 362 289 234	
10	2.13	2.16	35	+	-20.633 576 702 947 70	100
				-	20.633 546 884 399 75	
15	2.35	2.69	51	+	-50.841 387 284 381 90	150
				-	-50.841 387 284 185 84	
25	2.67	3.51	39	+	-149.219 456 142 191 3	50
				-	-149.219 456 142 191 0	
50	3.16	4.98	9	+	-615.020 090 902 757 6	20
				-	-615.020 090 902 757 6	
100	3.76	7.06	8	+	-2845.867 880 342 076	20
				-	-2845.867 880 342 076	

worked with the values summarized in Table I. This criterion is very simple and provides practically the same results as when we use the optimal values of the parameters.

It is interesting to study the dependence of the convergence of the method with the parameter of the potential, Z^2 . This can be seen by comparing the values of the number of the states considered in the basis (k_{\max}) and the perturbation order shown in Table I. Note that the values of these parameters increase for $1 < Z^2 < 25$ and are very small out of this range. The facts that the number of states needed to obtain convergence decreases and that the speed of convergence increases for $Z^2 > 50$ are explained by the adequacy of the basis set we use for the cases in which the double-well almost degenerates into two separated wells. The difficulty noted for intermediate values of Z^2 is explained as follows: For these values the zone between the two wells has important effects on the wave functions, which are difficult to obtain with our basis set. It is therefore necessary to use a large number of states to reproduce the appropriate behavior in this zone. Finally, we must note that if Z^2 is small, $Z^2 < 1$; then the harmonic oscillator basis set gives results very similar to those given by our basis set, and they may be even better than ours, as we shall see when we discuss the excited states.

V. EXCITED STATES

As we have already mentioned, our method cannot be applied to the rest of the excited states, at least in the

same way as that for the ground state. However, the excellent results obtained for the energies of the ground and first excited state for every value of Z^2 show that the perturbative-variational method of constructing the wave function gives us an excellent, almost exact, approximation for the eigenfunctions of these states. The mechanism of constructing these perturbative-variational wave functions for the rest of excited states is identical to the one used for the ground state, with a change of the state we use as the first-order approximation. It may be hoped that the right choice of the values of the variational parameters will allow us to get also good approximations to the eigenfunctions corresponding to those excited states.

The variational criterion will be strictly applicable to a set of trial wave functions for an excited state if we know exactly the eigenfunctions of all states with less energy

TABLE II. Overlap among the best approximation for different states obtained using the perturbative-variational method for different values of Z^2 .

Z^2	1	50	100
Overlap			
$ \langle 0 4\rangle $	1.30×10^{-16}	3.26×10^{-18}	1.33×10^{-18}
$ \langle 0 10\rangle $	1.62×10^{-12}	2.36×10^{-16}	1.90×10^{-21}
$ \langle 0 14\rangle $	1.76×10^{-13}	5.68×10^{-11}	1.04×10^{-19}
$ \langle 4 10\rangle $	1.45×10^{-11}	3.48×10^{-15}	1.44×10^{-18}
$ \langle 4 14\rangle $	3.53×10^{-13}	1.97×10^{-9}	1.16×10^{-17}
$ \langle 10 14\rangle $	1.03×10^{-15}	4.58×10^{-8}	1.92×10^{-9}

TABLE III. Energies obtained for different excited states (all with even parity) for the cases studied in Table II. They agree with the results obtained by using the method of Balsa *et al.* (Ref. 11).

Z^2	1	50	100
4	14.372 406 504 677 87	-575.385 717 351 526 8	-2429.480 313 186 997
10	46.969 968 159 901 75	-516.880 898 286 863 9	-2345.356 825 499 766
14	73.209 480 637 650 87	-478.537 623 684 984 0	-2289.584 227 545 887

and we require the trial wave function to be orthogonal to them. Obviously, the solutions of our approximation are not the exact solutions of the two-well anharmonic oscillator. However, it is interesting to note that the best solutions provided by our method for different states, without imposing orthogonality, are almost orthogonal to each other at least for a wide range of values of Z^2 as is shown in Table II. The values we obtain for the energy are in very good agreement with those obtained using the method of Balsa *et al.*¹¹ for all the significant figures shown in Table III. All these results permit us to affirm that the approximation to the wave functions for these excited states are rather adequate.

However, in the practical calculation of the excited states, we find that there are great difficulties for values of Z^2 between 10 and 25. In these cases, we are only able to approximate the two first states, and if we increase the number of the states in the basis set, there are problems of convergence. As a matter of fact, the difficulties only disappear for every excited state ($n < 25$) if $100 > Z^2 > 50$. These difficulties are explained if we look at Fig. 1. Here, we see that the importance of the states of the basis does not decrease quickly when we increase the value m of the

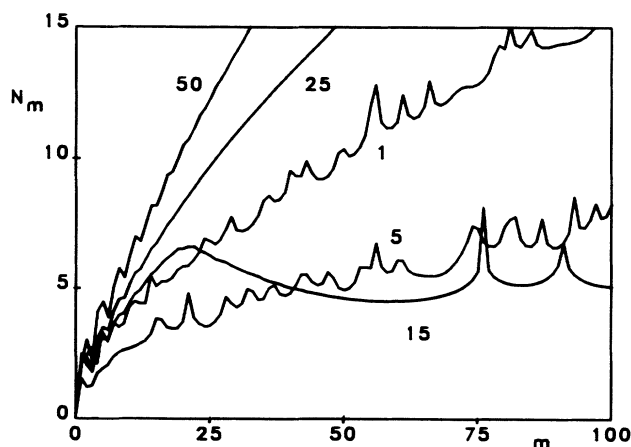


FIG. 1. Variation of the coefficients of the normalized ground state $C_{0,m}$ for different values of Z^2 is shown. With N_m , we have represented $-\log_{10}|C_{0,m}|$ as a function of m ; the numbers in the figure correspond to the values of Z^2 . We can see that $C_{0,m}$ decrease quickly when we increase m for both small and big values of Z^2 . This behavior disappears for intermediate values of Z^2 ($5 < Z^2 < 25$).

state for $10 < Z^2 < 25$. This problem disappears for other values of Z^2 and means that we must include a greater number of states in order to obtain a reasonable approximation for the state. This indicates that the basis set we use is not adequate for the range mentioned.

It is important to point out that for $Z^2 < 1$ the best results are obtained with $a=0$, that is, for harmonic-oscillator functions centered at the origin. The reason for this result is that for small values of Z^2 the rupture of the potential in two wells is not very important and can therefore be taken into account with use of a harmonic-oscillator basis set. However, the inclusion of the parameter a is necessary for large values of Z^2 ($Z^2 > 25$). So it is better to use $a=0$ for small values of Z^2 ($Z^2 < 1$) and $a \neq 0$ for large values. For intermediate values of Z^2 , $10 < Z^2 < 25$, neither of the two possibilities provides acceptable results, and the perturbative-variational method is not useful for the excited states.

VI. CONCLUSIONS

The main conclusion of this work is that the use of nonorthogonal basis set does not pose an additional problem in the construction of the perturbative-variational functions and in the application of the variational criterion for obtaining the eigenvalues. The only difficulty is the calculation of the matrix elements of the Hamiltonian, but this is common for the cases of orthogonal basis sets. The nonorthogonality of the basis set provides more flexibility for choosing the basis and for including the free parameters that we shall use for a specific problem.

The results obtained for the two-well anharmonic oscillator when we use a basis set of shifted harmonic functions is a good example of the advantages of working with a basis set that is adequate for the characteristics of the problem. A comparison with the results of Fernandez, Meson, and Castro,⁶ who use harmonic-oscillator functions shows that with our basis set we can use any value of Z^2 without problems and obtain excellent results with a faster convergence for the ground and first excited states. For the other excited states, the method presents great convergence difficulties for intermediate values of Z^2 . For greater values of Z^2 , $100 > Z^2 > 50$, the method provides results with an accuracy comparable to those obtained using Hill's determinants,¹¹ which have a high precision.

Finally, we would like to emphasize that the perturbative-variational method merges adequately the perturbation theory and variational method. The pertur-

bation theory allows one to generate an adequate set of trial wave functions simply and systematically; moreover, the variational approach provides the criterion for fixing the free parameters and a very good estimation of the eigenvalues. In this sense, it is important to point out that the perturbative-variational functions for different excited states are almost orthogonal to each other. This is remarkable in view of the fact that our basis set is

nonorthogonal and that the orthogonality has never been required.

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