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Variational and coupled-cluster calculations of the spectra of anharmonic oscillators

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Using the general anharmonic oscillator as a case study, we examine the coupled-cluster method (CCM) in some detail. Emphasis is specially placed on the accuracy of the standard ground-state energy calculation and the excitation spectrum as derived via the Emrich ansatz. We are particularly interested in problems that can arise from large differences between the exact wave function and its model counterpart that forms the starting point of the CCM. To this end we begin with a variational Hartree approximation applied to three particular anharmonic-oscillator Hamiltonians that contain, respectively, pure quartic, equally weighted cubic and quartic, and double-well perturbations. These are chosen to provide increasingly stringent tests for the CCM in the above sense. Considerable attention is paid to the variational description of the double-well case, where the various possible solutions to the Hartree equations are considered and a further calculation on the energy-level splitting is performed. The CCM is then used to improve systematically upon our chosen starting point and is shown, particularly for the ground state, both to produce extremely accurate results and to be rather resilient to even gross deficiencies in the starting wave function. The main problem is the double-well system, where the CCM shows its lack of intrinsic inbuilt tunneling mechanisms via the absence of level splitting. Even here the CCM still produces very accurate average energies for very deep wells. While clearly needing some modification in such extreme cases, the CCM is shown to be quite adaptable and robust with regard to inaccurate starting wave functions.

I. INTRODUCTION

The coupled-cluster method (CCM) is a very powerful technique for describing many-particle systems, which has been successfully applied to many different types of physical problems. Its original basis was the observation[1] that the exact interacting ground state of a many-body system could be usefully written as an exponential operator $\exp(S)$ acting on the noninteracting model state. What is gained from such a parametrization is that the perturbation or cluster expansion of the operator S then contains only linked terms. The reason for this lies ultimately with the nature of cumulant-type expansions for problems of a fundamentally probabilistic nature. The Ursell-Mayer cluster expansion in statistical mechanics is another classical example. Coester[2] and Coester and Kümmel[3] showed how the linked cluster operator S could be used as the generator of a similarity transformation for the exact ground-state problem, and thereby gave birth to what was originally called the $\exp(S)$ method of many-body theory, and what later became known as the CCM. The method has been fairly extensively reviewed in the literature,[4–8] and has also been widely applied.

Applications include problems in nuclear physics,[4,7] both for finite nuclei and infinite nuclear matter; atomic and molecular systems in quantum chemistry;[6,9–12] and the homogeneous electron liquid.[5,13–15] Recently, the domain of application of the CCM has been extended to two systems not normally associated with traditional many-body physics—namely, the anharmonic oscillator[16–18] and the ϕ^4 relativistic field theory (see Ref. 19 and Refs. 1–6 cited therein). In both of these latter applications the starting point has been a Bogoliubov-transformed model wave function, with coefficients that are determined variationally (and known variously as the Hartree or Gaussian approximation). CCM techniques have then been employed to improve systematically on this starting approximation.

In the present paper we first present in Sec. II a rather detailed analysis of the Hartree ansatz for a Hamiltonian that describes a rather general class of quantum anharmonic oscillators. We extend the previous work of Hsue and Chern[17] on the anharmonic oscillator with a pure quartic perturbation, by applying our chosen ansatz to two additional systems—namely, both one with equally weighted cubic and quartic perturbations (which allows us to produce a very asymmetric potential) and the standard symmetric double-well oscillator (with its nearly doubly degenerate energy levels in the case of a high central barrier). The latter system is of particular interest since, as is by now well known, it can in some sense be considered analogous to a ϕ^4-field theory in $(0+1)$ dimensions. A further variational calculation of the energy-level splitting is also performed for this system.

In Sec. III the CCM technique is then used to improve systematically on the preceding initial approximations. Earlier work concerned with the ground state[18] is first extended to the case of our more general Hamiltonian. The Emrich formalism[20,21] that has been employed in the standard many-body problem to extend the CCM to deal with excited states, is then employed here to discuss the excitation spectrum. In particular, we show how the excited-state equations can rather easily be obtained from their corresponding previous ground-state counterparts. We present and discuss detailed results for each of the three cases mentioned earlier. Our main aim is not simply to produce results of high numerical accuracy (since rather straightforward matrix diagonalization techniques[17,22] are, for such systems, often technically simpler and more accurate), but rather to assess the strengths and weaknesses of the standard CCM implementation for the ground and excited states of what are, as we shall see, rather challenging systems. In particular, we are interested in the applicability of the CCM to systems where the model or starting wave function is a poor approximation to the exact one.

II. VARIATIONAL APPROACH

A. Formalism

The fundamental system of interest to us here is the one-body anharmonic oscillator described by the Hamiltonian

$$H=\tfrac{1}{2}p^2+\tfrac{1}{2}x^2-\epsilon x^2+\gamma x^3+\lambda x^4 \ , \tag{2.1}$$

which can be equivalently written in the form

$$H=\tfrac{1}{2}+a^\dagger a-\tfrac{1}{2}\epsilon(a^\dagger+a)^2+2^{-3/2}\gamma(a^\dagger+a)^3 +\tfrac{1}{4}\lambda(a^\dagger+a)^4 \ , \tag{2.2}$$

where a and $a^\dagger$ are, respectively, the usual destruction and creation operators for the harmonic oscillator, with $a\equiv 2^{-1/2}(x+ip)$ and $a^\dagger$ is its Hermitian conjugate. We further define $|0\rangle$ to be the vacuum state for these operators, $a|0\rangle=0$, and as usual we have the standard commutation relation $[a,a^\dagger]=1$.

In common with previous work,[16–18] we start with the variational ansatz (equivalent to the Hartree approximation after optimization[17]),

$$|\phi\rangle=\exp(sa^\dagger+\tfrac{1}{2}ta^{\dagger 2})|0\rangle \ , \tag{2.3}$$

for our trial starting wave function, where s and t are c-number parameters yet to be determined. It is extremely convenient to perform the (most general linear) Bogoliubov transformation between the operators a and $a^\dagger$, defined as

$$b=c_1 a+c_2 a^\dagger+c_3 \tag{2.4}$$

and

$$b^\dagger=c_1 a^\dagger+c_2 a+c_3 \ , \tag{2.5}$$

with the proviso that $|\phi\rangle$ is now the new vacuum state for the new destruction operator b,

$$b|\phi\rangle=0 \ . \tag{2.6}$$

It is important to note that we have restricted ourselves from the outset to real parameters s and t in Eq. (2.3) and c_1, c_2, and c_3 in Eq. (2.4). We shall see explicitly later that this is not a serious limitation. Use of Eq. (2.6), together with the constraint that the transformation is a canonical one, namely $[b,b^\dagger]=1$, allows the three coefficients c_i in Eqs. (2.4) and (2.5) to be expressed in terms of the variational parameters s and t of Eq. (2.3). In this way we find the result that the Bogoliubov transformation may simply be regarded as a rotation plus translation of the original oscillator Hilbert space to the new oscillator space,

$$b=(1-t^2)^{-1/2}(a-ta^\dagger-s) \tag{2.7}$$

and

$$b^\dagger=(1-t^2)^{-1/2}(a^\dagger-ta-s) \ . \tag{2.8}$$

Before proceeding we make two observations concerning this transformation. In the first place, we see clearly the requirement $|t|<1$ for the transformation to be unitary. Secondly, the effect of the presence of the parameter s in Eq. (2.3) is to produce a translational shift Δx in the spatial coordinate x, given by

$$\Delta x=2^{1/2}s(1-t)^{-1} \ . \tag{2.9}$$

Thus the special case $s=0$ implies no translational shift.

By inverting the transformations (2.7) and (2.8),

$$a=(1-t^2)^{-1/2}(b+tb^\dagger)+s(1-t)^{-1} \ , \tag{2.10}$$

$$a^\dagger=(1-t^2)^{-1/2}(tb+b^\dagger)+s(1-t)^{-1} \ , \tag{2.11}$$

we can now readily express the Hamiltonian (2.2) in terms of the new operators b and $b^\dagger$. It is convenient to express it in normal-ordered form by making use of the simply proven relations,

$$\begin{aligned}(b+b^\dagger)^2&={:}(b+b^\dagger)^2{:}+1 \ ,\\ (b+b^\dagger)^3&={:}(b+b^\dagger)^3{:}+3(b+b^\dagger) \ ,\\ (b+b^\dagger)^4&={:}(b+b^\dagger)^4{:}+6{:}(b+b^\dagger)^2{:}+3 \ ,\end{aligned} \tag{2.12}$$

where ${:}\theta{:}$ represents the normal ordering with respect to b and $b^\dagger$ of the operator $\theta=\theta(b,b^\dagger)$. The resulting expression for H is more compactly given in terms of two new variables,

$$\omega\equiv(1-t)/(1+t), \quad \omega'\equiv s/(1-t) \tag{2.13}$$

as

$$\begin{aligned}H=E_0&+\left[\frac{1-\omega^2}{4\omega}\right](b^2+b^{\dagger 2})+\left[\frac{1+\omega^2}{2\omega}\right]b^\dagger b+\left[\frac{(1-2\epsilon)\omega'}{\omega^{1/2}}+\frac{\gamma}{2^{3/2}}\left[\frac{3}{\omega^{3/2}}+\frac{12\omega'^2}{\omega^{1/2}}\right]+\lambda\left[\frac{6\omega'}{\omega^{3/2}}+\frac{8\omega'^3}{\omega^{1/2}}\right]\right](b+b^\dagger)\\ &+\left[-\frac{\epsilon}{2\omega}+\frac{6\gamma\omega'}{2^{3/2}\omega}+\lambda\left[\frac{3}{2\omega^2}+\frac{6\omega'^2}{\omega}\right]\right]{:}(b+b^\dagger)^2{:}+\left[\frac{\gamma}{(2\omega)^{3/2}}+\frac{2\lambda\omega'}{\omega^{3/2}}\right]{:}(b+b^\dagger)^3{:}+\frac{\lambda}{4\omega^2}{:}(b+b^\dagger)^4{:} \ ,\end{aligned} \tag{2.14}$$

where the constant term E_0 is given by

$$E_0=\frac{(1-2\epsilon+\omega^2)}{4\omega}+\frac{3\lambda}{4\omega^2}+\frac{3\gamma\omega'}{2^{1/2}\omega}+\left[1-2\epsilon+\frac{6\lambda}{\omega}\right]\omega'^2+2^{3/2}\gamma\omega'^3+4\lambda\omega'^4 \; . \tag{2.15}$$

Using the fact that $b\,|\,\phi\rangle=0=\langle\phi\,|\,b^\dagger$ by the definition of Eq. (2.6), it is clear from Eq. (2.14) that our variational estimate of the ground-state energy $\langle\phi\,|\,H\,|\,\phi\rangle/\langle\phi\,|\,\phi\rangle$ is precisely equal to E_0. The expression (2.15) may now be extremized in the usual way with respect to ω and ω', thereby obtaining the two simultaneous equations for these quantities,

$$\omega^3-(1-2\epsilon+6\sqrt{2}\gamma\omega'+24\lambda\omega'^2)\omega-6\lambda=0 \tag{2.16}$$

and

$$(8\lambda\omega)\omega'^3+(3\sqrt{2}\gamma\omega)\omega'^2+[(1-2\epsilon)\omega+6\lambda]\omega'+3\gamma/2^{3/2}=0 \; . \tag{2.17}$$

We note that from Eqs. (2.9) and (2.13) the parameter ω' is directly proportional to the translational shift Δx induced by the transformation, $\omega'=\Delta x/2^{1/2}$.

In order to demonstrate the accuracy of the variational ansatz (2.3) for the trial wave function, we consider below three special cases of the Hamiltonian of Eq. (2.1). In each case the procedure is the same, namely, to solve the two simultaneous cubic equations (2.16) and (2.17) for ω and ω', and to insert these values into the expression (2.15) for the resulting variational bound on the ground-state energy.

B. Pure quartic anharmonicity: A symmetric perturbation

We first consider the case where $\epsilon=0=\gamma$ and $\lambda>0$ in the Hamiltonian (2.1), which produces a quartic anharmonic perturbation λx^4 of the harmonic oscillator, and which is clearly symmetric about the origin $x=0$. In this case (and indeed whenever $\gamma=0$) we see that Eq. (2.17) has $\omega'=0$ as a solution. It is also clear that since Eq. (2.17) is a cubic equation in the parameter ω', there are two other roots. These are of no interest here, since they correspond to pure imaginary values for ω' when we restrict ourselves to positive values of ω as required by the transformation to be unitary. These extra roots will be discussed, however, in the case of the symmetric double well considered below. Restricting ourselves to the solution $\omega'=0$, the remaining equation (2.16) for ω becomes

$$\omega^3-\omega-6\lambda=0 \; . \tag{2.18}$$

It is easy to see that Eq. (2.18) has exactly one real positive root, $\omega>0$, for each $\lambda>0$, and that only this root therefore corresponds to a unitary transformation $(\,|\,t\,|\,<1)$.

Numerical results are shown in Table I. As has been reported elsewhere for this case,[16] the variational ansatz gives very good results for the ground-state energy. The error is no greater than 2% over the entire range of λ considered, namely, $\lambda\leq 1000$. The fractional error increases as the strength of the anharmonicity increases, as is to be expected, although it approaches a value of about 2% for very large values of λ, where the Hamiltonian has become almost pure quartic in nature.

TABLE I. Comparison of the variational ground-state energy with its exact counterpart (taken from Ref. 17), for the quartic anharmonic oscillator of Eq. (2.1), with $\epsilon=0=\gamma$, and for various values of the coupling constant λ. Percentage errors are given in parentheses.

λ	Exact	Variational
0.1	0.559 15	0.5603(0.21)
1.0	0.803 77	0.8125(1.08)
10.0	1.504 97	1.5312(1.75)
100.0	3.131 38	3.1924(1.95)
1000.0	6.694 22	6.8279(2.00)

C. Cubic-plus-quartic anharmonicity: An asymmetric perturbation

We next consider the special case of the Hamiltonian of Eq. (2.1) with $\epsilon=0$ and $\gamma=\lambda>0$,

$$H=\tfrac{1}{2}p^2+\tfrac{1}{2}x^2+\lambda(x^3+x^4) \; , \tag{2.19}$$

which consists of equally weighted cubic and quartic anharmonic perturbations, as used by Hsue and Chern.[17] Since this potential is not symmetric about the origin, $x=0$, as shown in Fig. 1, we expect from the outset that our optimal transformation might produce a nonzero translational shift via a nonzero value of the parameter s (and hence also of ω'). Apart from the asymmetry about the origin, the potential of Eq. (2.19) has another special feature which is illustrated in Fig. 1. Thus for values of $\lambda>\frac{16}{9}$ (≈ 1.78) the potential develops a second minimum at some negative value of x, apart from the minimum at $x=0$, which is present for all values of λ. The two wells are generally of unequal depth, except for the special case $\lambda=2$, which is symmetric about $x=-\frac{1}{4}$, as shown in Fig. 1.

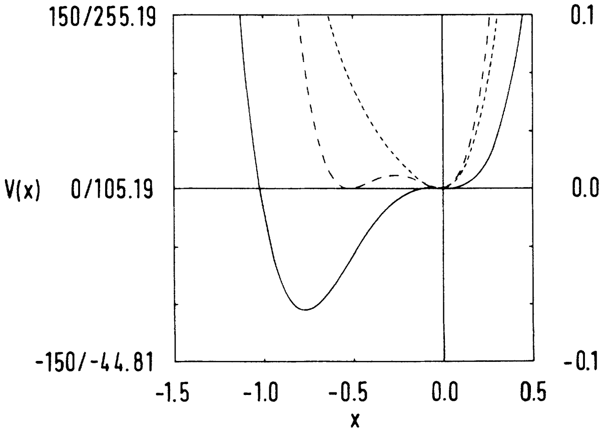

FIG. 1. Potential $V(x)=\frac{1}{2}x^2+\lambda(x^3+x^4)$ for three values of λ: 1000 (solid line), 2 (long-dashed line), and 1 (short-dashed line). Note the different scales on the right (for $\lambda=2$ and 1) and the left (for $\lambda=1000$). The $\lambda=1000$ scale is given as measured from $V=0$ and the potential minimum.

It is important to point out from the outset that, unlike the case of the symmetric double well to be considered below, the double-well feature here does not play a major role in the determination of the energy spectrum. Thus, for large values of λ, the secondary well (with the origin as its minimum) is very much shallower than the primary one. Indeed, on the scale of Fig. 1, the well at the origin cannot even be distinguished for the case $\lambda=1000$. On the other hand, for smaller values of λ, such as the $\lambda=2$ case shown in Fig. 1, the two-well nature is also relatively insignificant, since the ground-state energy lies far above the maximum separating the two wells. Thus the main general effect of the perturbation introduced in Eq. (2.19) is to produce an asymmetry in the potential.

Numerical results for the ground-state energy in this case are presented in Table II. We note that in principle Eqs. (2.16) and (2.17) have multiple pairs of solutions for ω and ω'. Although they are all guaranteed to be extrema of $E_0=E_0(\omega,\omega')$ of Eq. (2.15), they will naturally not all be local minima in general. They all provide, of course, variational bounds for the energy. In the present case, just as for the case of the pure quartic anharmonicity, the restriction to unitary transformations, along with the imposed reality of ω and ω', leads to a single solution for the (ω,ω') pair which is continuous over the entire range of the parameter λ considered.

As in the case of the pure quartic perturbation, the agreement with exact results is very good for reasonably small values of λ, and with the relative error initially increasing as λ is increased. The relative errors are, however, somewhat larger than in the previous case, with a value now approaching 5% for values of $\lambda\approx 100$. This relatively larger fractional error than in the previous case is undoubtedly a reflection of the fact that we are attempting to approximate a wave function which now is extremely far removed from that of a harmonic oscillator by one which is essentially tailored to the latter case. Considering the very large degree of asymmetric perturbation involved, it seems to us remarkable that the Hartree approximation still works so well.

When λ is further increased to values $\lambda\approx 1000$, the variational ansatz again improves, giving results accurate to about 1% and comparable to those obtained for values $\lambda\approx 0.5$. The explanation for this improvement in the accuracy is not difficult to find. We have already explained that the main feature of the present perturbing potential for large λ is the deep asymmetric well in the negative half of the x plane, as seen in Fig. 1 for the value $\lambda=1000$. The well for the case $\lambda=100$ actually looks very similar. The main difference between the two cases $\lambda=100$ and $\lambda=1000$ is the relative depth within the respective wells of the corresponding ground-state energy level. Thus, in the former case $\lambda=100$, the ground-state energy lies relatively farther from the bottom of the well, and the corresponding system in this state probes the asymmetric nature of the well rather more than in the case $\lambda=1000$, where the ground-state energy lies very near the bottom of the well. The system in the latter state thereby mostly probes the deep part of the well, which is closely approximated by a (shifted) harmonic oscillator. Since our ansatz (2.3) describes such situations precisely, the relatively smaller fractional error is understandable. We point out that the difference between the relative accuracy of our approximation for these two values of $\lambda(=100$ and $1000)$ illustrates a very important general point—namely, that a wave function with the proper symmetry will much more accurately be able to reproduce the ground-state energy of the system.

TABLE II. Comparison of the variational ground-state energy with exact results (calculated via the method of Ref. 17), for the quartic-plus-cubic anharmonic oscillator of Eq. (2.19), for various values of the coupling constant λ. Percentage errors are in parentheses. Note that all energies are measured from the potential minimum.

λ	Exact	Variational
0.1	0.553 52	0.5551(0.29)
1.0	0.720 46	0.7327(1.69)
2.0	0.791 30	0.8109(2.47)
10.0	1.6115	1.6766(3.78)
100.0	6.4927	6.8015(4.76)
200.0	9.6788	9.9570(2.87)
500.0	15.9174	16.159(1.52)
1000.0	22.897	23.123(0.99)

D. Symmetric double-well potential

As our final example, we consider the double-well quartic anharmonic oscillator in the specific form used by Balsa *et al.*,[22]

$$H=\tfrac{1}{2}(p^2-Z^2x^2+x^4)=\tfrac{1}{2}p^2+\tfrac{1}{2}(x^2-\tfrac{1}{2}Z^2)^2-Z^4/8\ , \tag{2.20}$$

which can be obtained from our original Hamiltonian of Eq. (2.1) by the choices $\epsilon=\frac{1}{2}(1+Z^2)$, $\gamma=0$, and $\lambda=\frac{1}{2}$.

For this potential the solutions to Eqs. (2.16) and (2.17) divide conveniently into the following two cases.

Case 1: $\omega'=0$. It is clear that Eq. (2.17) permits the solution $\omega'=0$ whenever $\gamma=0$, and for this root the remaining equation (2.16) for ω reduces to

$$\omega^3+Z^2\omega-3=0\ . \tag{2.21}$$

Case 2: $\omega'\neq 0$. The (reduced) equation (2.17) for ω' now becomes

$$\omega'^2=(Z^2\omega-3)/4\omega\ . \tag{2.22}$$

When Eq. (2.22) is inserted into Eq. (2.16), one can readily show that the equation for ω reduces to

$$\omega^3-2Z^2\omega+6=0\ , \tag{2.23}$$

and a combination of Eqs. (2.22) and (2.23) further shows that the corresponding associated solutions for ω' are

$$\omega'=\pm 2^{-3/2}\omega\ . \tag{2.24}$$

Since the shift Δx produced by our Bogoliubov transformation is proportional to ω', it is clear that the case-1 wave functions correspond to states centered around $x=0$; whereas in the corresponding case 2, there are two states produced for each root ω of Eq. (2.23), which are shifted from the origin as center and are simply mirror reflections of each other. These parity doublets are evidently degenerate in energy as clearly seen from Eq. (2.15), which is an even function of ω' when $\gamma=0$.

It may be useful at this point to enumerate carefully the number of states that our procedure has produced. In principle, case 1 will produce three states, one for each of the three roots of Eq. (2.21). In practice, only those roots which correspond to a parameter $|t|<1$, and which hence produce a unitary Bogoliubov transformation, are allowed. Just as in the previous two examples, it turns out again that there is only one such case-1 root, which is real and continuous over the range of values of Z^2 considered.

The situation for case 2 is more complicated. The corresponding (real and imaginary parts of the) three roots of Eq. (2.23) are displayed in Fig. 2 as a function of Z^2. The real negative root $\omega<0$ present for all Z^2 produces a nonunitary transformation ($|t|>1$) and can hence immediately be discarded. The two remaining roots are both real and positive (and hence acceptable) for $Z^2>Z_c^2=3^{5/3}/2(\approx 3.1201)$. Conversely, for $Z^2<Z_c^2$ the two remaining roots form a complex conjugate pair. Such roots are in principle quite acceptable, although we remind the reader that for the sake of simplicity our analysis to date has assumed real values for the variational parameters. It would be quite possible to redo our analysis with this restriction removed, but in the present case this is not necessary since we shall find that the case-2 double roots lead to bounds E_0 for the ground-state energy, which are energetically disfavored relative to the case-1 root for values of Z^2 less than a certain crossover value which is somewhat *greater* than Z_c^2. It is for this reason that we do not pursue the analysis further in the case of complex roots, since the merit of simplicity is needlessly lost, at least for present purposes.

In summary, case 1 produces one viable wave function centered about $x=0$, and case 2 produces two pairs of viable wave functions for $Z^2>Z_c^2$, with each pair being a degenerate parity doublet, one of which is shifted to the left of the origin and the other of which is shifted symmetrically to the right. The corresponding three variational bounds E_0 to the ground-state energy from Eq. (2.15) are displayed in Fig. 3 for both the case-1 wave function and both sets of case-2 wave functions for $Z^2>Z_c^2$, and comparison is also made with the exact result over the range $0\leq Z^2\leq 10$. The exact result has been calculated by the method described by Balsa *et al.*[22] In Table III we also compare both the case-1 energy and the lower of the two case-2 energies with the exact result. This table quotes both the percentage error in comparison with the exact result and the ratios of the various energies to the height, $V_p=Z^4/8$, of the mid-well peak between the maximum at $x=0$ and the two minima. We note also that all of the results in Fig. 3 and Table III have been shifted upwards by the amount $Z^4/8$, which then renders the Hamiltonian of Eq. (2.20) positive definite.

We see that for Z^2 greater than some crossover value of approximately 3.4, one of the two shifted case-2 parity doublets produces the lowest energy, and for $Z^2\gtrsim 5$ it compares very favorably with the exact result. The variational calculation in this case is clearly seen to improve as the ground-state energy level sits deeper inside the double well (as measured by the ratio E/V_p quoted in Table III), as is to be expected. We see that for $E/V_p\lesssim\frac{1}{4}$ the accuracy is better than 1%. It is also interesting to compare the translational shifts $\pm\Delta x$ produced by our case-2 variational wave functions with the positions $\pm x_{\min}$ $(=\pm 2^{-1/2}Z)$ of the two minima in the potential. One sees clearly from the results shown in Table IV that as Z^2 increases, the translational shift approaches the position of the minimum more and more closely. Indeed, in the limit as $Z^2\rightarrow\infty$, our variational ansatz with this corresponding case-2 solution describes the ground state of this system exactly as that of a harmonic oscillator separated by an infinitely high barrier from another identical harmonic oscillator infinitely far away.

In the converse case where Z^2 is less than the crossover value of approximately 3.4, the case-1 wave function

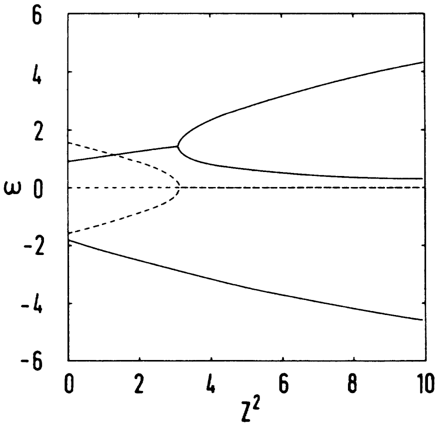

FIG. 2. Real (solid lines) and imaginary (dashed lines) parts of the three roots of Eq. (2.23), as a function of the coupling parameter Z^2. The nonzero imaginary roots correspond to the two roots in the upper half of the plane, after their real parts become equal. The solution whose real part lies in the lower half of the plane is, in fact, real throughout.

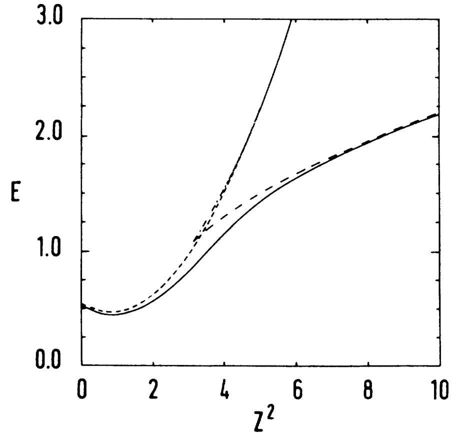

FIG. 3. Case-1 (short-dashed line), case-2 (higher energy) (dot-dashed line), and case-2 (lower energy) (long-dashed line) ground-state energies, along with the exact answer (solid line), for Z^2 from 0 to 10. Note that all energies have been shifted by a factor of $Z^4/8$, rendering the energy positive semidefinite.

TABLE III. Ground-state energies for case-1 and case-2 (lower energy) wave functions versus the exact answer for the symmetric double well. Also displayed are the ratios of the energy to the central peak of the potential and the percentage error. Note that all energies are measured relative to the potential minimum.

	Exact		Case 2			Case 1		
Z^2	E	E/V_p	E	E/V_p	%	E	E/V_p	%
50	4.9899	0.016	4.9925	0.016	0.04	208.4	0.67	
15	2.7043	0.096	2.7131	0.096	0.32	18.800	0.67	
10	2.1832	0.17	2.1972	0.18	0.64	8.408	0.67	
7	1.7895	0.29	1.8138	0.30	1.35	4.1891	0.68	
5	1.4199	0.45	1.4972	0.48	5.44	2.229	0.71	60.0
4	1.1448	0.57	1.3027	0.65	13.8	1.5103	0.75	31.9
3.8	1.0822	0.60	1.2587	0.70	16.3	1.3882	0.77	28.3
3.6	1.0184	0.63	1.2120	0.75	19.0	1.2733	0.79	25.0
3.4	0.9542	0.66	1.1620	0.80	21.8	1.1658	0.81	22.2
3.2	0.8905	0.70	1.1066	0.86	24.3	1.0657	0.83	19.7
Z_c^2	0.8654	0.71	1.0817	0.89	25.0	1.0278	0.84	18.8
3	0.8282	0.74				0.9731	0.86	17.5
2	0.5689	1.14				0.6250	1.25	9.86
1	0.4538	3.63				0.4770	3.82	5.11
0.5	0.4663	14.9				0.4818	15.4	3.34
0	0.5302	∞				0.5408	∞	2.00

centered on $x=0$ has the lowest energy. We see from Table III that this occurs when the exact ground-state energy lies higher than about two-thirds of the height of the central peak. As already mentioned earlier, this crossover point occurs at a value of $Z^2 > Z_c^2$. It is clear that the region $3 \lesssim Z^2 \lesssim 4$ is not described well by either the shifted or unshifted variational wave function, with even the better producing errors of the order of 20% in this region. However, as soon as Z^2 decreases below a value of about 2, such that the ground-state energy now lies above the central peak of the potential, the accuracy of the case-1 wave function shows a dramatic increase.

We see from these results a first indication of the very important observation that the absence of tunneling in our model wave functions can give rise to large errors in regions where such tunneling may physically be expected to become important. Before proceeding, as in Sec. III, to consider how systematically to improve upon the various variational wave functions considered to date by CCM techniques, we first consider further the present double-well case and the consequent energy-level splitting due to tunneling between the wells.

TABLE IV. Position of the minimum in the positive well vs case-2 translational shift for the symmetric double-well potential.

Z^2	$x_{\min}$	Δx
50	5	4.9849
15	2.7386	2.6872
10	2.2361	2.1569
7	1.8708	1.7527
5	1.5811	1.4018
4	1.4142	1.1644
3.8	1.3784	1.1051
3.6	1.3416	1.0380
3.4	1.3038	0.9574
3.2	1.2649	0.8425
Z_c^2	1.2490	0.7211

E. Variational calculation of energy splitting

In situations such as those that arise from the case-2 wave functions above for the symmetric double-well potential, where we have a degenerate pair of wave functions, it seems worthwhile to attempt some calculation for the level splitting. We consider the general case, where, for some particular Hamiltonian of the form of Eq. (2.1), the variational trial wave function of the form of Eq. (2.3) has two different parametrizations which produce the same minimum energy. We denote these two (normalized) states as $|\psi_1\rangle$ and $|\psi_2\rangle$ and define the quantities

$$\epsilon_0 \equiv \langle \psi_1 | H | \psi_1 \rangle = \langle \psi_2 | H | \psi_2 \rangle , \tag{2.25}$$

$$\Omega \equiv \langle \psi_1 | \psi_2 \rangle , \tag{2.26}$$

and

$$\Delta \equiv \langle \psi_1 | H | \psi_2 \rangle . \tag{2.27}$$

We may then define a variationally improved wave function $|\psi\rangle$ as the linear combination

$$|\psi\rangle \equiv |\psi_1\rangle + \alpha |\psi_2\rangle . \tag{2.28}$$

The variational estimate for the energy associated with the new trial wave function is then given by

$$E \equiv \frac{\langle \psi | H | \psi \rangle}{\langle \psi | \psi \rangle} = \frac{\epsilon_0(1+|\alpha|^2) + \alpha\Delta + \alpha^*\Delta^*}{1+|\alpha|^2 + \alpha\Omega + \alpha^*\Omega^*} . \tag{2.29}$$

In general, we could now treat α and α^* as independent variational parameters. In keeping with our earlier restriction to trial wave functions of the form of Eq. (2.3) with real parameters s and t, we now restrict ourselves for ease to the case where α, Ω, and Δ are all real. The extremization of Eq. (2.29) with respect to the parameter α then gives the result

$$(\alpha^2-1)(\Omega\epsilon_0-\Delta)=0 \ . \tag{2.30}$$

Thus, unless $\epsilon_0=\Delta/\Omega$ (in which case either $|\psi_1\rangle=|\psi_2\rangle$, or either one is an exact ground-state wave function), the variation imposes the condition $\alpha=\pm 1$, which leads to the two states

$$|\pm\rangle=|\psi_1\rangle\pm|\psi_2\rangle \ , \tag{2.31}$$

with corresponding variational estimates for the energy as

$$E_\pm=\frac{\epsilon_0\pm\Delta}{1\pm\Omega} \ . \tag{2.32}$$

We now apply the above to the case where the two variationally degenerate unnormalized ground-state wave functions $|\phi_1\rangle$ and $|\phi_2\rangle$ both have the form of Eq. (2.3), namely,

$$|\phi_i\rangle=\exp(s_i a^\dagger+\tfrac{1}{2}t_i a^{\dagger 2}), \quad i=1,2 \tag{2.33}$$

and where the parameters s_i and t_i are again restricted to be real from the outset, for ease of presentation. We now construct the overlap integral of these two wave functions in the form

$$\langle\phi_1|\phi_2\rangle=\exp[-\tfrac{1}{2}(s_1^2/t_1+s_2^2/t_2)]J(s_1,s_2;t_1,t_2) \ , \tag{2.34}$$

where the quantity J is defined as

$$J(s_1,s_2;t_1,t_2)\equiv\langle 0|\exp[\tfrac{1}{2}t_1(a+s_1/t_1)^2]\exp[\tfrac{1}{2}t_2(a^\dagger+s_2/t_2)^2]|0\rangle \ . \tag{2.35}$$

Rather than attempting a direct evaluation of the quantity J, we now develop a functional relation for it which we can then solve iteratively. Proceeding anew from Eq. (2.33) we write the overlap integral $\langle\phi_1|\phi_2\rangle$ as

$$\langle\phi_1|\phi_2\rangle=\langle 0|e^{(1/2)t_1a^2}(e^{s_1a}e^{s_2a^\dagger}e^{-s_1a})(e^{s_1a}e^{(1/2)t_2a^{\dagger 2}}e^{-s_1a})e^{s_1a}|0\rangle \ , \tag{2.36}$$

by simply inserting the identity operator $I=\exp(-s_1a)\exp(s_1a)$ twice. We now make use of the fact that $a|0\rangle=0$ and evaluate the two bracketed terms in Eq. (2.36) with the aid of the simply proven general result

$$e^{s_1a}f(a^\dagger)e^{-s_1a}=f(a^\dagger+s_1) \ , \tag{2.37}$$

for an arbitrary function $f(a^\dagger)$, to write Eq. (2.36) as

$$\langle\phi_1|\phi_2\rangle=\langle 0|Ie^{(1/2)t_1a^2}e^{s_2(a^\dagger+s_1)}e^{(1/2)t_2(a^\dagger+s_1)^2}|0\rangle \ . \tag{2.38}$$

We may again insert into Eq. (2.38) an identity operator of the form

$$I=\exp(s_2a^\dagger)\exp(-s_2a^\dagger)$$

at the place so indicated. Then, by using $\langle 0|a^\dagger=0$, together with the analogue of Eq. (2.37), namely,

$$e^{-s_2a^\dagger}f(a)e^{s_2a^\dagger}=f(a+s_2) \ , \tag{2.39}$$

we find, by comparison with Eq. (2.35), the result

$$\langle\phi_1|\phi_2\rangle=e^{s_1s_2}J(s_2t_1,s_1t_2;t_1,t_2) \ . \tag{2.40}$$

A comparison of Eqs. (2.34) and (2.40) leads to the functional relation

$$J(s_1,s_2;t_1,t_2)=\exp\left[\frac{s_1^2}{2t_1}+\frac{s_2^2}{2t_2}+s_1s_2\right]J(s_2t_1,s_1t_2;t_1,t_2) \ . \tag{2.41}$$

By making the replacements $s_1\to s_2t_1$ and $s_2\to s_1t_2$ in Eq. (2.41), it is a simple matter to derive the further relation

$$J(s_1,s_2;t_1,t_2)=\exp\left[(1+t_1t_2)\left[\frac{s_1^2}{2t_1}+\frac{s_2^2}{2t_2}+s_1s_2\right]\right]J(s_1t_1t_2,s_2t_1t_2;t_1,t_2) \ . \tag{2.42}$$

By repeatedly iterating Eq. (2.42), with a rescaling of each variable $s_i\to s_it_1t_2$ at each step, we find

$$\begin{aligned}J(s_1,s_2;t_1,t_2)=&\exp\left[[1+t_1t_2+(t_1t_2)^2+\cdots+(t_1t_2)^{2n-1}]\left[\frac{s_1^2}{2t_1}+\frac{s_2^2}{2t_2}+s_1s_2\right]\right]\\&\times J(s_1(t_1t_2)^n,s_2(t_1t_2)^n;t_1,t_2) \ .\end{aligned} \tag{2.43}$$

By taking the limit as $n \rightarrow \infty$ of Eq. (2.43) we find simply

$$J(s_1,s_2;t_1,t_2)=\exp\left[\left(\frac{s_1^2}{2t_1}+\frac{s_2^2}{2t_2}+s_1s_2\right)\times(1-t_1t_2)^{-1}\right]\times J(0,0;t_1,t_2),\quad |t_1t_2|<1\ . \tag{2.44}$$

The final evaluation of $J(0,0;t_1,t_2)$ is easily done directly from the definition of Eq. (2.35), by expanding the exponentials to give

$$\begin{aligned}J(0,0;t_1,t_2)&=\langle 0|e^{(1/2)t_1a^2}e^{(1/2)t_2a^{\dagger 2}}|0\rangle\\&=\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{1}{m!}(\tfrac{1}{2}t_1)^m\frac{1}{n!}(\tfrac{1}{2}t_2)^n\\&\quad\times\langle 0|a^{2m}(a^\dagger)^{2n}|0\rangle\ .\end{aligned} \tag{2.45}$$

The remaining evaluation of Eq. (2.45) is trivially performed, with the result

$$\begin{aligned}J(0,0;t_1,t_2)&=\sum_{n=0}^{\infty}\frac{(2n)!}{(n!)^2}\left[\frac{t_1t_2}{4}\right]^n\\&=(1-t_1t_2)^{-1/2},\quad |t_1t_2|<1\ .\end{aligned} \tag{2.46}$$

The final result for the overlap integral is then obtained from Eqs. (2.34), (2.44), and (2.46) as

$$\begin{aligned}\langle\phi_1|\phi_2\rangle=(1-t_1t_2)^{-1/2}&\exp[(\tfrac{1}{2}s_1^2t_2+\tfrac{1}{2}s_2^2t_1+s_1s_2)\\&\times(1-t_1t_2)^{-1}],\ |t_1t_2|<1\ .\end{aligned} \tag{2.47}$$

We note that the restriction $|t_1t_2|<1$ is necessary for the overlap integral to be finite. In particular, we also see that the previously mentioned restriction, $|t|<1$, in connection with the Bogoliubov transformation (2.7) being unitary, is necessary for wave functions of the form of Eq. (2.3) to be normalizable.

We now specialize further to the case of most interest to us, namely, the degenerate parity doublets corresponding to the case-2 double-well wave functions of Sec. II D. These have the form $s_1=-s_2\equiv s$, $t_1=t_2\equiv t$,

$$\begin{aligned}|\phi_R\rangle&=\exp(sa^\dagger+\tfrac{1}{2}ta^{\dagger 2})|0\rangle\ ,\\|\phi_L\rangle&=\exp(-sa^\dagger+\tfrac{1}{2}ta^{\dagger 2})|0\rangle\ .\end{aligned} \tag{2.48}$$

Using the result of Eq. (2.47) we may now immediately calculate the overlap integral Ω of Eq. (2.26) as

$$\Omega\equiv\frac{\langle\phi_R|\phi_L\rangle}{(\langle\phi_R|\phi_R\rangle\langle\phi_L|\phi_L\rangle)^{1/2}}=\exp\left[-\frac{2s^2}{1-t^2}\right], \tag{2.49}$$

and where the restriction $|t|<1$ is again understood to hold. The same method that enabled us to evaluate the overlap integral $\langle\phi_1|\phi_2\rangle$ also can easily be extended to give the result for the quantity

$$\langle\phi_1|\text{''}P(a,a^\dagger)\text{''}|\phi_2\rangle\ ,$$

where $P=P(x,y)$ is an arbitrary polynomial in x and y, and the notation "θ" indicates antinormal ordering of the operator $\theta=\theta(a,a^\dagger)$ with respect to the arguments a and $a^\dagger$. Thus we have from Eq. (2.33) the result

$$\langle\phi_1|a^m(a^\dagger)^n|\phi_2\rangle=\left[\frac{\partial}{\partial s_1}\right]^m\left[\frac{\partial}{\partial s_2}\right]^n\langle\phi_1|\phi_2\rangle\ , \tag{2.50}$$

which can be combined with our fundamental relation (2.47) to obtain the desired quantities. In this way we may readily also calculate the remaining quantity Δ of Eq. (2.27). If the Hamiltonian of Eq. (2.2), for the case $\gamma=0$ of present interest, is first expressed in antinormal-ordered form as

$$H=H_0+H_1aa^\dagger+H_2\text{''}(a+a^\dagger)^2\text{''}+H_4\text{''}(a+a^\dagger)^4\text{''}\ , \tag{2.51}$$

then it is not difficult to show that the corresponding quantity Δ of Eq. (2.27), calculated with the states of Eq. (2.48), can be given as

$$\begin{aligned}\Delta&\equiv\frac{\langle\phi_R|H|\phi_L\rangle}{(\langle\phi_R|\phi_R\rangle\langle\phi_L|\phi_L\rangle)^{1/2}}\\&=\left\{H_0+\frac{H_1}{1-t^2}\left[1-s^2\left[\frac{1-t}{1+t}\right]\right]\right.\\&\quad\left.+\frac{2H_2}{1-t}+\frac{12H_4}{(1-t)^2}\right\}\Omega\ .\end{aligned} \tag{2.52}$$

By making use of the simply proven relations

$$\begin{aligned}(a+a^\dagger)^2&=\text{''}(a+a^\dagger)^2\text{''}-1\ ,\\(a+a^\dagger)^4&=\text{''}(a+a^\dagger)^4\text{''}-6\text{''}(a+a^\dagger)^2\text{''}+3\ ,\end{aligned} \tag{2.53}$$

we may simply relate the coefficients H_i in Eq. (2.51) to the coupling constants of the symmetric double-well Hamiltonian of Eq. (2.20), or more generally of Eq. (2.2) in the case $\gamma=0$,

$$\begin{aligned}H_0&=-\tfrac{1}{2}+\tfrac{1}{2}\epsilon+3\lambda/4,\quad H_1=1\ ,\\H_2&=-\tfrac{1}{2}\epsilon-3\lambda/2,\quad H_4=\lambda/4\ .\end{aligned} \tag{2.54}$$

By making use of Eqs. (2.32), (2.49), and (2.52) we may now consider the splitting of the lowest energy level for the example of the double-well potential of Eq. (2.20), through the application of these techniques to the degenerate case-2 parity doublets of Sec. II D that produced the lower energy in the case $Z^2>Z_c^2$. Results are presented in Table V for the exact ground and first excited states E_0 and E_1 (and their splitting, $\Delta E\equiv E_1-E_0$) of the Hamiltonian $H+Z^4/8$ of Eq. (2.20); and a comparison is made with our corresponding variational estimates $E_\pm$ of Eq. (2.32) calculated as described. A comparison with the corresponding results in Table III immediately shows a marked improvement in the corresponding estimates for the ground-state energy E_0, in those cases where the tunneling phenomenon is important. In the case of very deep wells where the tunneling is very small, our estimate $|E_+-E_-|$ for the splitting ΔE is generally too small. However, in the very important regime

TABLE V. Comparison of variational (V) and exact (E) energy eigenvalues for the ground and first excited states, and level splitting, for the symmetric double-well potential. Note that all energy values are measured relative to the minimum of the potential. Percentage errors are given in parentheses.

Z^2	E,V	E_0	E_1	ΔE
50	E	4.9899	4.9899	0
	V	4.9925(0.04)	4.9925(0.04)	0
15	E	2.7043	2.7043	10^{-10}
	V	2.7131(0.32)	2.7131(0.32)	10^{-15}
10	E	2.1832	2.1832	1.49×10^{-5}
	V	2.1972(0.64)	2.1972(0.64)	1.25×10^{-7}
7	E	1.7895	1.7938	4.33×10^{-3}
	V	1.8135(1.34)	1.8141(1.13)	5.95×10^{-4}
5	E	1.4199	1.4997	0.080
	V	1.4738(3.39)	1.5207(1.40)	0.047(−41.2)
4	E	1.1448	1.3760	0.2312
	V	1.1902(3.97)	1.4252(3.58)	0.235(1.64)
3.8	E	1.0822	1.3573	0.275
	V	1.1177(3.28)	1.4199(4.61)	0.302(9.82)
3.6	E	1.0184	1.3413	0.323
	V	1.0440(2.51)	1.4202(5.88)	0.376(16.4)
3.4	E	0.9542	1.3285	0.374
	V	0.9762(2.31)	1.4254(7.29)	0.449(20.0)
3.2	E	0.8905	1.3192	0.429
	V	0.9312(4.57)	1.4342(7.96)	0.503(17.2)
Z_c^2	E	0.8654	1.3166	0.4512
	V	0.9515(9.95)	1.4448(9.74)	0.4933(9.33)

$3 \lesssim Z^2 \lesssim 4$, where the tunneling is particularly important, the estimated splitting is rather accurate. We note also that in principle the calculation could be further improved by varying the energy estimates with respect to ω and ω' after constructing the improved symmetric and antisymmetric wave functions. We do not, however, believe that this will lead to a significant further increase in accuracy.

We note also that since the states $|\phi_R\rangle$ and $|\phi_L\rangle$ are linearly independent, the general theory of variational calculations with respect to wave functions which are linear combinations of linearly independent functions[23] shows that as well as the smaller of our two eigenvalues $E_\pm$ being an upper bound to E_0 the larger is also an upper bound to E_1. These bounds are clearly observed from the numerical comparisons with the exact results in Table V. Unfortunately, no such boundedness property pertains to the splitting ΔE, which appears to be underestimated for large Z^2 (small tunneling), but to be slightly overestimated when the tunneling becomes more appreciable.

III. COUPLED-CLUSTER METHOD

A. Formalism

The intention in the remainder of this paper is now to use the CCM to improve in a systematic fashion on the variational approach of Sec. II. We do this in the standard fashion[2–8] by starting from the variationally determined wave function $|\phi\rangle$ of Eq. (2.3) as our zeroth-order approximation. Using the fact that $|\phi\rangle$ is the vacuum with respect to the canonically transformed operator b, from Eq. (2.6), we then build up the exact (unnormalized) ground-state wave function $|\psi\rangle$ of the anharmonic oscillator in the standard CCM fashion by explicitly constructing the higher-order correlations as

$$|\psi\rangle = e^{\hat{S}}|\phi\rangle \, , \tag{3.1}$$

where the operator $\hat{S}$ is given by

$$\hat{S} = \sum_{n=1}^{\infty} \hat{S}_n \tag{3.2}$$

and

$$\hat{S}_n = S_n (b^\dagger)^n \, . \tag{3.3}$$

The exact ground-state wave function $|\psi\rangle$ is thus exactly parametrized by the set of parameters $\{S_n \mid n = 1,2,\ldots\}$. We note that neither state $|\phi\rangle$ nor $|\psi\rangle$ is normalized as defined, although $\langle\phi|\psi\rangle = \langle\phi|\phi\rangle$.

The exact ground-state Schrödinger equation,

$$H|\psi\rangle = E|\psi\rangle \, , \tag{3.4}$$

may now be decomposed in the standard CCM fashion, by premultiplication with the operator $\exp(-\hat{S})$ followed by projection onto the states $\langle\phi|$ and $\langle\phi|b^n$, with $n=1,2,\ldots$, to give, respectively, an equation for the exact ground-state energy,

$$E=\langle\phi|He^{\hat{S}}|\phi\rangle/\langle\phi|\phi\rangle\ , \tag{3.5}$$

and an infinite coupled hierarchy of equations for the parameters $\{S_n\}$,

$$\langle\phi|b^n(e^{-\hat{S}}He^{\hat{S}})|\phi\rangle=0,\quad n=1,2,\ldots\ . \tag{3.6}$$

In order to evaluate Eqs. (3.5) and (3.6) explicitly it is useful to express our basic Hamiltonian of Eq. (2.1) in the somewhat more general normal-ordered form

$$H=\sum_{i=0}^{4}\sum_{j=0}^{4-i}h_{ij}(b^\dagger)^i b^j\ . \tag{3.7}$$

The parameters h_{ij} can be related to those in the standard form of Eq. (2.1) by making use of Eqs. (2.14) and (2.15),

$$\begin{aligned}
&h_{00}=E_0\ ,\\
&h_{01}=h_{10}=\frac{3\gamma}{(2\omega)^{3/2}}+\left[\frac{(1-2\epsilon)}{\omega^{1/2}}+\frac{6\lambda}{\omega^{3/2}}\right]\omega'+\frac{6\gamma}{(2\omega)^{1/2}}\omega'^2+\frac{8\lambda}{\omega^{1/2}}\omega'^3\ ,\\
&h_{02}=h_{20}=(1-\omega^2)/4\omega+\chi,\ \ h_{11}=(1+\omega^2)/2\omega+2\chi\ ,\\
&\chi\equiv-\frac{\epsilon}{2\omega}+\frac{3\lambda}{2\omega^2}+\frac{6\gamma}{2^{3/2}\omega}\omega'+\frac{6\lambda}{\omega}\omega'^2\ ,\\
&h_{03}=h_{30}=\frac{\gamma}{(2\omega)^{3/2}}+\frac{2\lambda}{\omega^{3/2}}\omega',\ \ h_{12}=h_{21}=3h_{03}\ ,\\
&h_{04}=h_{40}=\lambda/4\omega^2,\ \ h_{13}=h_{31}=4h_{04},\ \ h_{22}=6h_{04}\ .
\end{aligned} \tag{3.8}$$

We note in passing that when the values of ω and ω' that extremize E_0 are used, from the solutions to Eqs. (2.16) and (2.17), the linear terms disappear ($h_{01}=0=h_{10}$) and the quadratic terms are diagonalized ($h_{02}=0=h_{20}$; $h_{11}=\omega$), as is expected in the Hartree approximation to which our variational method corresponds.

Insertion of Eq. (3.7) into Eq. (3.5) then gives

$$E=h_{00}+\sum_{j=1}^{4}j!h_{0j}S_j+h_{02}S_1^2+6h_{03}S_1S_2+12h_{04}(S_2^2+2S_1S_3)+h_{03}S_1^3+12h_{04}S_1^2S_2+h_{04}S_1^4 \tag{3.9}$$

for the ground-state energy in terms of the parameters $\{S_n\}$. These parameters in turn are to be calculated from the coupled set of multinomials which arise from the insertion of Eq. (3.7) into Eq. (3.6). A very lengthy calculation, employing the well-known nested commutator expansion for the term in parentheses in Eq. (3.6), leads to the result

$$\begin{aligned}
&\sum_{i=0}^{4}h_{i0}\delta_{in}+(n+4)(n+3)(n+2)(n+1)h_{04}S_{n+4}+(n+3)(n+2)(n+1)h_{03}S_{n+3}\\
&\quad+(n+2)(n+1)(h_{02}+nh_{13})S_{n+2}+(n+1)(h_{01}+nh_{12})S_{n+1}+n[h_{11}+(n-1)h_{22}]S_n\\
&\quad+(n-1)h_{21}S_{n-1}+(n-2)h_{31}S_{n-2}\\
&\quad+\sum_{k,l}kl\{[2(k-1)(k-2)+3(k-1)(l-1)+2(l-1)(l-2)]h_{04}\delta_{k+l,\,n+4}+\tfrac{3}{2}(k+l-2)h_{03}\delta_{k+l,\,n+3}\\
&\qquad\quad+[h_{02}+\tfrac{3}{2}(k+l-2)h_{13}]\delta_{k+l,\,n+2}+h_{12}\delta_{k+l,\,n+1}+h_{22}\delta_{k+l,\,n}\}S_kS_l\\
&\quad+\sum_{k,l,m}klm[2(k+l+m-3)h_{04}\delta_{k+l+m,\,n+4}+h_{03}\delta_{k+l+m,\,n+3}+h_{13}\delta_{k+l+m,\,n+2}]S_kS_lS_m\\
&\quad+\sum_{j,k,l,m}jklmh_{04}\delta_{j+k+l+m,\,n+4}S_jS_kS_lS_m=0,\quad n=1,2,\ldots
\end{aligned} \tag{3.10}$$

and where (for the cases $n=1,2$) we interpret $S_0 \equiv S_{-1} \equiv 0$. A simpler version of Eq. (3.10), corresponding to the special case of the Hamiltonian (2.1) with $\epsilon=0=\gamma$, was first reported by Kaulfuss and Altenbokum.[18]

The excited states $|\psi'\rangle$ and their corresponding eigenenergies E',

$$H|\psi'\rangle = E'|\psi'\rangle \ , \tag{3.11}$$

may also be found within the CCM by using the Emrich[20,21] parametrization for excited states,

$$|\psi'\rangle = \hat{S}' e^{\hat{S}}|\phi\rangle = \hat{S}'|\psi\rangle \ , \tag{3.12}$$

where $\hat{S}$ is the same ground-state correlation operator as in Eqs. (3.1)–(3.3), and the new excitation correlation operator $\hat{S}'$ has a similar decomposition,

$$\hat{S}' = \sum_{n=1}^{\infty} \hat{S}'_n \ , \tag{3.13}$$

and

$$\hat{S}'_n = S'_n (b^\dagger)^n \ . \tag{3.14}$$

A simple combination of the ground- and excited-state Schrödinger equations readily gives the result

$$[H,\hat{S}']|\psi\rangle = (E'-E)\hat{S}'|\psi\rangle \ . \tag{3.15}$$

The excitation parameters $\{S'_n\}$ may now similarly be obtained by projecting Eq. (3.15) onto the states $\langle\phi|b^n \exp(-\hat{S})$,

$$\frac{\langle\phi|b^n(e^{-\hat{S}}[H,\hat{S}']e^{\hat{S}})|\phi\rangle}{n!\langle\phi|\phi\rangle} = (E'-E)S'_n, \quad n=1,2,\ldots \ . \tag{3.16}$$

We note that once the nonlinear ground-state equations (3.10) for the parameters $\{S_n\}$ are solved, they are simply input for the excitation equations (3.16). These equations are then a coupled set of linear eigenvalue equations for the excitation parameters $\{S'_n\}$, with eigenvalues which directly give the excitation energies $(E'-E)$. Furthermore, once we have evaluated the ground-state equations (3.6), their excited-state counterparts (3.16) are very easily derived from them. Thus by using the nested commutator expansions for the respective term in parentheses in the left-hand side of both equations we see the clear symmetry discussed by Emrich,[20,21] which amounts to replacing each multinomial in the $\{S_n\}$ arising from the expansion of the left-hand side of Eq. (3.6) with a corresponding set of terms in which each single S_i is replaced one at a time in turn by the corresponding S'_i, and the zeroth-order term in the $\{S_n\}$ is dropped. Very explicitly, since Eq. (3.10) is derived from Eq. (3.6) by dividing throughout by the same expression $(n!)\langle\phi|\phi\rangle$ as appears in the denominator in Eq. (3.16), the left-hand side of Eq. (3.16) may be obtained from the corresponding left-hand side of Eq. (3.10) by (i) dropping the (zeroth-order) first term completely, (ii) replacing each S_i by S'_i in the linear terms, (iii) replacing the product $S_k S_l$ by $(S'_k S_l + S_k S'_l)$, or equivalently by $2S'_k S'_l$, in the quadratic terms, (iv) replacing the product $S_k S_l S_m$ by $(S'_k S_l S_m + S_k S'_l S_m + S_k S_l S'_m)$, or equivalently by $3S'_k S_l S_m$, in the cubic terms, and (v) replacing the product $S_j S_k S_l S_m$ by the analogous sum of terms, or equivalently by $4S'_j S_k S_l S_m$, in the quartic term.

In principle, the CCM equations (3.9) and (3.10), and the excited-state counterpart of the latter equation derived as above from Eq. (3.16), provide two infinite hierarchies of equations that yield the exact ground- and excited-state energies and wave functions. In practice, however, it is clear that an approximation scheme is needed. In the case of the ground-state equations (3.10), the simplest and most natural such scheme is the so-called SUB(n) approximation in which all S_i with $i>n$ are set to zero, and the lowest n coupled equations are then solved consistently. Similarly, the excited-state equations derived from Eq. (3.10) as already described are truncated in the so-called SUB(m,n) scheme, where again the S'_j with $j>m$ are set to zero and the lowest m coupled linear eigenvalue equations are solved consistently for the lowest m excited states; and where the corresponding ground-state input parameters $\{S_i\}$ are obtained from solving Eq. (3.10) at the SUB(n) level of approximation.

Before proceeding to our numerical results, it is necessary to address the question of multiple solutions to Eqs. (3.10) in the SUB(n) approximation. Their general structure is that of a coupled set of multinomials. If we regard the ith equation in the SUB(n)-truncated hierarchy as determining the parameter S_i itself, then the order in S_i of the ith equation is 3 for $i=1$ or 2, 2 for $i=3$ or 4, and 1 for $i>4$. It is clear that numerous solutions exist in general, at each level of truncation for the set $\{S_i\}$. There are various ways that one can envisage to choose a particular solution. For example, Kaulfuss and Altenbokum[18] perform a stability analysis on their solutions for the pure quartic anharmonic oscillator by introducing temperature dependence and requiring stability against thermal fluctuations.

In the present paper we adopt a more direct approach. As usual (for bound states), we first restrict our set of solutions to those wherein all of the S_i parameters are real. The equations are then solved numerically, using the hybrid Powell method[24] which utilizes the Jacobian in determining successive approximations. Henceforth we refer to this method of solution as method 1. The only ambiguity is in choosing the starting point for the successive approximation scheme. A natural starting point is to set all $S_i=0$, and this will generally produce a solution which is in some (admittedly rather ill-defined) sense "closest" to our starting variational wave function. [We note in passing that because in Eq. (3.10) $h_{10}=0=h_{20}$, when we start as here from the Hartree approximation the SUB(1) approximation produces a solution $S_1=0$ and the SUB(2) approximation produces a solution $S_1=0=S_2$.] We note that this simple choice reproduces, for example, all of the data presented by Kaulfuss and Altenbokum[18] using their thermodynamic stability analysis.

Another way to proceed is to iterate Eq. (3.10) in the SUB(n) approximation one or more times, by solving the

ith equation as a polynomial equation in the corresponding parameter S_i. One may either continue this procedure iteratively until convergence is obtained at the desired level of accuracy, or until one decides to break it at some point and then use these approximate solutions in the hybrid Powell scheme. We shall refer to the straightforward iterative procedure as method 2. This method 2 is naturally capable of producing multiple solutions as, for example, we solve the cubic equations for S_1 and S_2 and the quadratic equations for S_3 and S_4. Indeed, we have used this procedure to accelerate the convergence of method 1 by performing one iteration with method 2 first, and choosing at every opportunity the real root of smallest absolute magnitude. Wherever checked, this has always led to the same solution as the $S_i = 0$ starting point, which in turn reproduces all of the quartic anharmonic data which was presented by Kaulfuss and Altenbokum using their thermodynamic stability criterion. We thus choose the procedure as outlined above as our standard method of solution and, except where explicitly noted, all of the data presented were obtained by isolating a particular ground-state set of parameters $\{S_i\}$ in the corresponding SUB(n) approximation in this manner. Finally, we remind the reader that there is no further uncertainty (in the sense of a multiplicity of solutions) in the excited-state equations, since these are

TABLE VI. Exact results for the ground and first four excited states of the quartic anharmonic oscillator, for several values of the coupling constant λ, compared with those calculated via the CCM, with various SUB(m,m) approximation. All energies are measured from the potential minimum.

λ	m	E_0	E_1	E_2	E_3	E_4
0.1	exact	0.559 15	1.769 50	3.138 62	4.628 88	6.220 30
0.1	2	0.560 31	1.781 50	3.203 86		
0.1	4	0.559 18	1.768 39	3.134 65	4.802 33	6.640 42
0.1	6	0.559 14	1.769 31	3.136 97	4.623 48	6.237 61
0.1	8	0.559 15	1.769 50	3.138 44	4.621 92	6.202 88
0.1	10	0.559 15	1.769 51	3.138 66	4.627 41	6.213 38
0.1	12	0.559 15	1.769 50	3.138 65	4.628 90	6.219 36
0.1	14	0.559 15	1.769 50	3.138 63	4.629 02	6.220 71
0.1	16	0.559 15	1.769 50	3.138 62	4.628 94	6.220 65
0.1	18	0.559 15	1.769 50	3.138 62	4.628 89	6.220 42
0.1	20	0.559 15	1.769 50	3.138 62	4.628 88	6.220 30
1.0	exact	0.803 77	2.737 89	5.179 29	7.942 40	10.9636
1.0	2	0.812 50	2.812 50	5.562 50		
1.0	8	0.803 71	2.736 81	5.165 80	7.854 29	10.8754
1.0	18[a]	0.803 77	2.737 83	5.179 65	7.961 18	11.0526
1.0	20[b]	0.803 77	2.737 77	5.178 10	7.955 29	11.0787
10.0	exact	1.504 97	5.321 61	10.3471	16.0901	22.4088
10.0	2	1.531 25	5.531 25	11.4062		
10.0	8	1.504 65	5.315 57	10.2831	15.8324	22.3149
10.0	16[a]	1.505 02	5.322 58	10.3680	16.1899	22.4253
10.0	20[b]	1.504 99	5.319 74	10.3316	16.3363	25.1474[c]
100.0	exact	3.131 38	11.1872	21.9069	34.1825	47.7072
100.0	2	3.192 44	11.6663	24.3181		
100.0	8	3.130 54	11.1712	21.7438	33.5969	47.6027
100.0	16[a]	3.131 53	11.1905	21.9720	34.4516	47.6289
100.0	20[b]	3.131 48	11.1802	21.8325	35.1731	47.8227[c]
1000.0	exact	6.694 22	23.9722	47.0173	73.4191	102.516
1000.0	2	6.827 95	25.0175	52.2743		
1000.0	4	6.710 91	23.8629	47.1529	86.9994	133.125
1000.0	6	6.693 52	23.8646	46.4855	75.0964	110.707
1000.0	8	6.692 33	23.9361	46.6531	72.1438	102.344
1000.0	10	6.693 23	23.9732	46.8968	71.8270	99.1747
1000.0	12	6.693 98	23.9852	47.0638	72.3808	98.5224
1000.0	14	6.694 39	23.9852	47.1491	73.1816	99.4460
1000.0	16[a]	6.694 57	23.9798	47.1692	74.0286	102.276
1000.0	18[b]	6.694 59	23.9708	47.1149	74.9300	114.311[c]
1000.0	20[b]	6.694 44	23.9548	46.8184	75.9196	99.6477[c]

[a] Highest SUB(m,m) entry without an imaginary pair in the excitation spectrum.

[b] SUB(m,m) entry with imaginary values in the excitation spectrum.

[c] Level has an imaginary component.

TABLE VII. Percentage errors of the first excited state for the quartic-perturbation anharmonic oscillator, for $\lambda = 100$, calculated via CCM in the SUB(m,n) approximation.

$n \backslash m$	2	4	6	8	10	12	14	16	18	20
2	4.28	0.80	1.29	1.55	1.60	1.60	1.59	1.59	1.59	1.59
4	2.67	−0.45	0.01	0.38	0.51	0.52[a]	0.51[a]	0.49[a]	0.48[a]	0.48[a]
6	2.30	−0.85	−0.43	−0.47	0.09	0.12[b]	0.10[b]	0.08[b]	0.06[b]	0.05
8	2.24	−0.93	−0.51	−0.14	1.3×10^{-3}	0.03	0.01[b]	−0.02[b]	−0.04[b]	−0.05[b]
10	2.25	−0.93	−0.50	−0.13	4.7×10^{-3}	0.03	0.01	−0.02[b]	−0.04[b]	−0.06[b]
12	2.26	−0.92	−0.49	−0.11	0.03	0.05	0.03	7.2×10^{-4}	−0.03[b]	−0.05[b]
14	2.27	−0.91	−0.48	−0.10	0.05	0.07	0.05	0.02	−0.01[b]	−0.05[b]
16	2.27	−0.91	−0.47	−0.09	0.06	0.08	0.06	0.03	−0.01[b]	−0.05[b]
18	2.28	−0.90	−0.47	−0.09	0.06	0.09	0.07	0.03	−0.01[b]	−0.05[b]
20	2.28	−0.90	−0.47	−0.09	0.06	0.09	0.07	0.03[b]	−0.01[b]	−0.06[b]

[a] Excitation spectrum contains complex values at the very top of the spectrum.

[b] Excitation spectrum contains at least one complex-conjugate pair.

simply a coupled set of linear eigenvalue equations in the parameters S_j' in the corresponding SUB(m,n) approximation already described.

In the remainder of this section, we now apply the CCM as described to the three particular anharmonic oscillators already studied variationally in Sec. II. In each case the variational wave functions that were determined there to extremize the ground-state energy are now used as our zeroth-order starting wave function $|\phi\rangle$. We note that the CCM has been applied previously[18] only in the ground-state formulation, and only then to the case of the pure quartic anharmonic oscillator.

B. Pure quartic anharmonicity

The exact results[17] for the ground and first four excited states of the quartic anharmonic oscillator of Sec. II B are compared with our CCM results in Table VI for various "diagonal" SUB(m,m) truncations with $2 \le m \le 20$. We note that in this case where the potential energy is symmetric about the origin, and the ground state thereby is a parity eigenstate, the odd-indexed amplitudes S_n vanish identically. Overall, the results are very encouraging. For small values of the quartic coupling constant λ, the results are extremely accurate. Thus the ground-state energy E is already obtained to five-digit accuracy at the SUB(8) level of approximation. As is to be expected, the higher states are not reproduced quite as accurately, although the first three or four excited states are obtained to a similar level of accuracy (i.e., a few parts in 10^6) in the SUB(20,20) approximation.

For larger values of the coupling constant λ, the situation is still very good. The ground-state energy in the SUB(n) approximation rapidly approaches very close to the exact value as n is increased to values as small as about 6, but then tends to oscillate slowly about the exact value with a marked decrease in the rate of convergence thereafter, as has been previously reported.[18] The excited states also exhibit similar convergence patterns. This behavior is clearly exhibited in Tables VII and VIII, which

TABLE VIII. Percentage errors of the fourth excited state for the quartic-perturbation anharmonic oscillator, for $\lambda = 100$, calculated via CCM in the SUB(m,n) approximation.

$n \backslash m$	2	4	6	8	10	12	14	16	18	20
2		35.1	5.90	−1.95	−3.05	−2.03	−0.94	−0.43	−0.38	−0.50
4		29.4	10.2	1.34	−1.24	−1.03[a]	0.32[a]	1.83[a]	2.87[a]	3.22[a]
6		28.3	7.79	1.05	−1.62	−1.81[b]	−0.77[b]	0.75[b]	2.23[b]	3.31
8		28.1	7.00	−0.22	−2.48	−2.74	−1.85[b]	−0.45[b]	1.02[b]	2.34[b]
10		28.2	6.85	−0.73	−3.20	−3.43	−2.62	−1.27[b]	0.21[b]	1.45[b]
12		28.2	6.86	−0.87	−3.50	−3.75	−2.91	−1.49	0.12[b]	1.12[b]
14		28.2	6.91	−0.86	−3.58	−3.85	−2.81	−1.03	1.54[b]	3.93[b]
16		28.2	6.96	−0.80	−3.56	−3.83	−2.62	−0.16	5.56[b]	1.69[c]
18		28.2	7.00	−0.72	−3.49	−3.76	−2.40	0.74	12.8[c]	−2.73[c]
20		28.2	7.04	−0.61	−3.35	−3.63	−2.15	1.64[b]	13.3[c]	0.24[c]

[a] Excitation spectrum contains complex values at the very top of the spectrum.

[b] Excitation spectrum contains at least one complex-conjugate pair.

[c] Level contains an imaginary component.

display the percentage deviations from the exact results for the first and fourth excited states. respectively, in the strong-coupling case $\lambda=100$ and for various SUB(m,n) approximations. Figure 4 also presents similar data for the first excited state in the form of an isometric projection. Table VII and Fig. 4 show quite clearly the behavior of the SUB(m,n) approximations to the first excited state. For a fixed value of n, an increase in index m produces again a rapid initial convergence, followed by slow oscillations, just as for the ground-state scheme. There is some indication, for the lower n values, that convergence does hold, although not precisely to the exact result.

If, on the other hand, we keep m fixed and increase the index n, this pattern of convergence to a value which is not precisely the exact result is even more apparent. Thus an increase in the index n with m fixed produces increasingly accurate results up to about the SUB(m,m) level. Further increases in the ground-state index n then produce essentially no further changes in the excitation energy.

We remark that this pattern of convergence is basically to be expected, since our method of evaluating the excitation energies from Eq. (3.15) means that these quantities only converge in principle to the exact results as *both* indices m and n approach infinity. Thus a finite truncation in either index leaves either the absolute excited-state or ground-state energy approximated. We note that this is *not*, however, true for the absolute excited-state energies if these were to be calculated from Eqs. (3.11) and (3.12) directly. Here, even if $\hat{S}$ is approximated at the SUB(n) level, convergence to the exact excited-state energies will be obtained in principle by continually increasing the truncation index m for the corresponding operator $\hat{S}'$. We return to this point in our concluding remarks in Sec. IV.

Finally, on the question of convergence, we note from Table VIII that the same basic pattern applies to the fourth excited state as to the first. The main difference is that to see similar effects one now needs to go to correspondingly higher levels of truncation, as is to be expected.

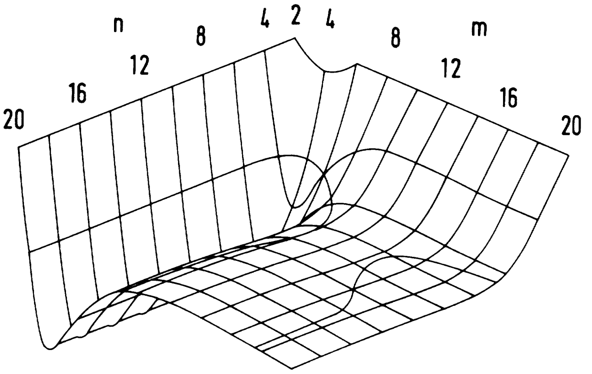

FIG. 4. Isometric projection of the percentage error of the CCM first excited state, calculated via the SUB(m,n) approximation. The error ranges between 1.0% and -0.93%, with the zero-error plane marked with a solid line.

We also comment briefly on the choice of "compatible" pairs of truncation indices (m,n), which has been discussed elsewhere by one of us[25] in the context of linear response theory. Thus one would like to know, for example, whether for a given index n, higher values of the index m in the SUB(m,n) truncation scheme necessarily lead to a better approximation. Such questions are difficult to answer without further information, and it was in this sense that the theory of linear response was shown[25] to provide a bridge between the otherwise somewhat disconnected ground- and excited-state CCM formalisms already discussed. Turning to the data presented in Tables VII and VIII, it is clear that a direct comparison with exact results does not obviously favor SUB(m,n) approximations with $m\approx n$ as one might at first thought expect to be favored. It is quite striking to note from Table VIII that the SUB$(m,2)$ approximations are already as accurate for the fourth excited state, as for calculations with the ground-state input taken from SUB(n) approximations with values of n even much higher than 2. One should note, however, that this is not true for the lower excited states, where an improvement in the ground-state approximation used as input to the excited-state formalism does lead to a noticeably improved value of the first few excitation energies, as seen from Table VII.

Tables VI–VIII also indicate another possible cause of concern that can arise in practical implementations via Eq. (3.16) of the Emrich formalism for excited states—namely, the appearance of complex eigenvalues in the energy excitation spectrum for intermediate and large values of the quartic anharmonicity. One should not, however, be surprised at the appearance of complex energy eigenvalues at a given level of approximation since the CCM approach is certainly not manifestly Hermitian. In particular, the matrix generated from Eq. (3.16) in the SUB(m,n) approximation, and regarded in the manner already discussed as a set of linear eigenvalue equations for the excitation amplitudes $\{S'_m\}$, is certainly *not* Hermitian.

Very little can be said in general about the reality or otherwise of the eigenvalues of non-Hermitian matrices associated with such eigenvalue problems. Of course, in the limit as $m,n\rightarrow\infty$, Eq. (3.16) will produce the exact, real excitation spectrum, but as we have previously noted this is not the case for any finite truncation in either index. Since Eq. (3.16) yields the difference between the excited- and ground-state energies, the best that we can expect, since the associated eigenvalue problem is non-Hermitian, is that if both the approximations to the ground and to the excited states are good, then the excitation energies produced by Eq. (3.16) will be both real and accurate. Conversely, if either approximation breaks down, one might expect that one signal of this breakdown may be the appearance of complex eigenvalues in the energy excitation spectrum.

We should briefly discuss the nature of these complex eigenvalues. Since Eq. (3.16) is an eigenvalue equation with real coefficients, any complex roots must arise as complex conjugate pairs. Let us consider some fixed SUB(m,n) approximation, and some value of the coupling parameter λ, such that this truncation produces only real eigenvalues for the excitation energies. As the parameter λ is increased, we find in general that a critical value occurs, beyond which a complex conjugate pair of eigenvalues appears as two previously real roots come together and then become complex. For example, in the SUB(20,20) approximation, and at a value $\lambda = 0.9$, Eq. (3.16) produces only real eigenvalues, but the twelfth and thirteenth excitation energies are equal to 59.05 and 60.52, respectively. As λ is increased to 0.91, these same two levels have become a complex conjugate pair, equal to $60.02 \pm 1.25i$, at the same level of approximation. The imaginary components will obviously start out small, but as λ is further increased beyond the critical value at which the complex roots first appear, the magnitude of the imaginary components will increase.

We have indicated in Tables VI–VIII those calculations which have produced at least one such complex conjugate pair of excitation energy eigenvalues. We have also specifically labeled those entries which have an imaginary component, though the value of this imaginary component is not itself shown. In all cases, only the real part is shown. For example, Table VI shows that at a coupling constant $\lambda = 1.0$, complex energy values first appear in the SUB(20,20) approximation. In this particular case only the 12th and 13th excited states have complex energy eigenvalues. The magnitude of the imaginary components is still only about 8% of the corresponding real component. We reiterate that the presence of such imaginary components has nothing to do with rounding errors or other numerical shortcomings of the calculations. They are, rather, a consequence of the method itself, as described above.

The trends in the appearance of the complex eigenvalues largely follow what one would expect. It is most convenient to consider these approximations in the three-dimensional parameter space of m, n, and λ. For calculations suitably "near the origin" in this space (i.e., for small λ, m, and n), no complex pairs occur in the excitation spectrum. If both λ and n are held fixed, and m is increased, there generally comes some point beyond which complex energies are produced. Further, these complex values usually occur near the top of the excitation spectrum so produced. This behavior is as expected, since by the Emrich parametrization for excited states of Eq. (3.12), we have built the excited states by further correlations built upon the CCM ground state. We thus tacitly assume that for a low-order approximation to work well, the important correlations in the ground state are largely shared by the excited states. This assumption is more likely to be valid for the low-lying excited states than for those higher in the spectrum. As the parameter m is increased further, one generally sees more and more states developing imaginary components to their energy eigenvalues. At the same time, the overall quality of the approximation to the energy spectrum then worsens. We also note from Table VI that an increase in λ produces more complex eigenvalues at a given SUB(m,n) level of approximation. This is again expected, since we know that as the strength of the anharmonicity increases, our approximations for both the ground and excited states worsen.

In conclusion, we should emphasize, however, that overall the Emrich parametrization for the excited states within the CCM works very well indeed. For small values of λ, the first excited-state energy is produced with nearly the same accuracy as that of the ground state. The next few levels are also almost as accurate. As the value of λ increases, we need to go to higher levels of truncation to achieve results of similar quality, as is to be expected. Even the spectra with imaginary components still produce some eigenvalues which are very accurate. One should probably view the possibility of Eq. (3.16) producing complex excitation energies as a help rather than a hindrance. Thus the appearance of complex eigenvalues is an internal signal of a breakdown in the approximation; and this could clearly be important in other applications of the method to systems where exact results are not known.

C. Cubic-plus-quartic anharmonicity

In Table IX we present the SUB(m,m) results for the asymmetric anharmonic oscillator potential considered previously in Sec. II C, and consisting of equally weighted cubic and quartic anharmonicities, as given in Eq. (2.19). The overall quality of the results is quite similar to the previous case of the pure quartic anharmonic perturbation. The ground-state CCM again does very well in all cases, even in the region around $\lambda = 100$, which was the most difficult for the variational approach of Sec. II. Whereas the variational energy had an error of about 5% for $\lambda = 100$, the SUB(20) ground state now has an error of about $10^{-3}\%$ for the energy. The overall pattern in the errors of the ground-state energies at a given SUB(n) level of truncation follows very closely that observed in the variational approach. Thus as λ increases initially, the accuracy drops due to the increasing asymmetry in the potential. For very large values of λ the error again decreases, as is observed in the $\lambda = 1000$ results in Table IX, since the ground state is now essentially sampling only a small, almost symmetric region near the minimum in the potential well.

The asymmetric nature of this potential also has a rather marked effect on the CCM excitation spectrum. Thus, in addition to the general decrease in accuracy with increasing excitation energy that we have already noted for the purely symmetric quartic potential, here we have now also to contend with the increasing degree of asymmetry of the potential which is sampled by the higher levels. This is particularly apparent in the $\lambda = 1000$ results in Table IX. One observes from Fig. 1 that whereas the ground state in this case samples an almost symmetric potential field, the excited states experience higher and higher levels of asymmetry. The third and fourth excited states clearly demonstrate this behavior. We remark again that the overall quality of the results for this asymmetric potential is also very encouraging.

The pattern for the appearance of complex eigenvalues for the excitation energies produced by the CCM Eq. (3.16) is similar to the case of the quartic anharmonic potential. There is, however, one important new observation. We again see that as λ increases, and the accurate reproduction of the energy spectrum in general becomes a correspondingly more stringent test of a given CCM truncation scheme, so complex conjugate pairs begin to occur at lower levels of truncation. This is clearly seen in Table IX for the SUB(m,m) approximations up to values of $\lambda = 100$. The $\lambda = 1000$ case is different however. Here the ground-state energy is reproduced very accurately at low approximations, but the higher excited states are clearly seen to require higher values of the truncation index. This behavior is also as observed for the lower values of λ. What is new in the $\lambda = 1000$ results is that no complex eigenvalues are now produced by Eq. (3.16) at similar levels of truncation. These observations are taken to indicate that the source of the complex conjugate pairs in the spectra for lower values of λ is more likely to arise from errors in the CCM ground state, and hence the associated correlation operator $\hat{S}$, rather than from a poor description of the excited states themselves via the operator $\hat{S}'$.

In summary, we see that the CCM ground-state formalism reproduces well, and at low levels of truncation, the energies of the ground states in even the most asymmetric potential wells considered. The Emrich parametrization of the excited states also works well, partic-

TABLE IX. Exact results for the ground and first four excited state of the quartic-plus-cubic anharmonic oscillator of Eq. (2.19), for several values of the coupling constant λ, compared with those calculated via the CCM, with various SUB(m,m) approximations. All energies are measured from the potential minimum.

λ	m	E_0	E_1	E_2	E_3	E_4
0.1	exact	0.553 52	1.745 51	3.095 40	4.567 64	6.142 15
0.1	1	0.555 14	1.761 51			
0.1	2	0.555 14	1.757 53	3.177 98		
0.1	3	0.554 69	1.748 31	3.156 02	4.812 61	
0.1	4	0.553 57	1.744 60	3.091 61	4.726 79	6.642 19
0.1	6	0.553 51	1.745 35	3.092 94	4.560 55	6.178 25
0.1	8	0.553 51	1.745 50	3.095 03	4.561 27	6.122 29
0.1	10	0.553 52	1.745 51	3.095 43	4.566 57	6.131 59
0.1	20	0.553 52	1.745 51	3.095 40	4.567 63	6.142 18
1.0	exact	0.720 46	2.501 36	4.838 68	7.508 76	10.4455
1.0	1	0.732 67	2.598 49			
1.0	8	0.720 32	2.498 84	4.809 90	7.390 59	10.4009
1.0	17[a]	0.720 48	2.501 24	4.846 66	7.573 48	10.4746
1.0	20[b]	0.720 47	2.500 73	4.834 82	7.586 24	11.4977
2.0	exact	0.791 30	2.879 79	5.727 91	9.003 42	12.6233
2.0	1	0.810 86	3.027 52			
2.0	8	0.790 95	2.873 02	5.664 70	8.829 61	12.6806
2.0	15[a]	0.791 33	2.881 24	5.754 87	9.054 69	11.9706
2.0	20[b]	0.791 39	2.868 69	5.511 00	8.880 52	11.4145
10	exact	1.611 49	4.716 79	9.274 07	14.5847	20.512
10	1	1.676 56	5.121 51			
10	8	1.609 11	4.698 96	9.000 08	14.2035	21.7047
10	13[a]	1.611 51	4.734 33	9.359 65	14.1451	17.6297
10	20[b]	1.611 33	4.700 87	9.061 75	13.8618	21.3181[c]
100	exact	6.492 65	14.4196	22.2608	32.578	44.280
100	1	6.801 49	18.8940			
100	8	6.492 14	14.3490	21.5670	30.300	43.247
100	12[a]	6.492 63	14.4284	22.2207	31.496	41.308
100	20[b]	6.492 74	14.4244	22.2982	32.521	43.109
1000.0	exact	22.897	64.81	98.24	116.2	134.5
1000.0	1	23.123	68.16			
1000.0	2	23.123	66.37	116.5		
1000.0	3	22.903	65.23	105.1	168.2	
1000.0	4	22.898	64.92	103.0	146.4	229.5
1000.0	6	22.897	64.83	99.87	135.5	182.4
1000.0	8	22.897	64.81	98.90	127.7	166.0
1000.0	10	22.897	64.81	98.47	122.8	154.0
1000.0	20	22.897	64.81	98.26	116.1	125.7

[a] Highest SUB(m,m) entry without an imaginary pair in the excitation spectrum.

[b] SUB(m,m) entry with imaginary values in the excitation spectrum.

[c] Level has an imaginary component.

ularly for the lower-lying excitations, although for the most asymmetric potentials the method is beginning to experience difficulties not previously encountered. The overall quality of the results remains impressive, however, particularly for relatively low values of the truncation parameters.

D. Symmetric double-well potential

In Fig. 5 we present the results of our CCM calculations for the symmetric double-well Hamiltonian of Eq. (2.20), which we investigated earlier in Sec. II D. The CCM data displayed are obtained by starting with the zeroth-order (uncorrelated) variational wave functions of both the case-1 and case-2 (lower-energy) types discussed in detail in Sec. II D. The case-2 (lower-energy) wave function is henceforth simply referred to as the case-2 wave function. The results shown, which cover a range of values of Z^2 with $0<Z^2\leq 50$ for case 1 and $Z_c^2\leq Z^2\leq 50$ for case 2, were calculated using the SUB(14) approximation for the ground state and the SUB(14,14) truncation for the excited states.

We first note that the overall quality of the ground-state results is again good. For the case 1, which we recall corresponds to a wave function centered at the origin, $x=0$, the CCM produces a very accurate value for the ground-state energy for values of the coupling constant Z^2 approximately up to the point where the mid-well potential maximum becomes higher than the ground-state energy level. This occurs at a value of $Z^2\approx 2$, at which point the corresponding error in the variational energy was about 10%. Even increasing Z^2 to somewhat higher values gives energies which are quite good. Thus even at $Z^2=Z_c^2$ the variational error of about 19% is reduced to about 3% in this CCM approximation. Of course, if Z^2 is increased still further, the CCM calculations based on the now increasingly bad starting approximations of the case-1 type, rapidly deteriorate. For such values of $Z^2\gtrsim Z_c^2$ we expect the CCM calculations based on the case-2 wave functions to be more accurate, since the case-2 wave functions are now shifted towards one of the potential minima, as discussed previously. The results of Fig. 5 clearly bear out this expectation. Good results are now found for the ground-state energy in the deep double-well potentials, at least by comparison with the *average* energy of the now nearly degenerate exact ground and first excited states. We still, apparently, totally miss the effects of tunneling. This pattern of CCM results built upon the case-2 wave functions holds for values of Z^2 as small as approximately 4.

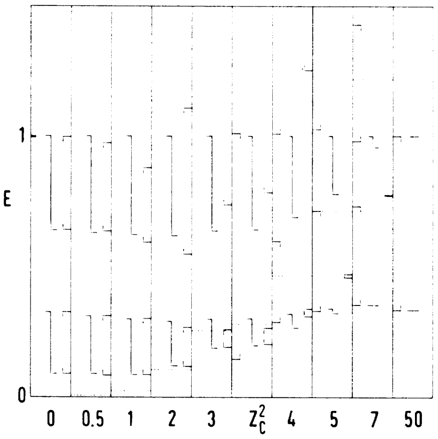

FIG. 5. Results for the double-well anharmonic oscillator for various values of Z^2. All energies have been normalized so that the exact third excited state is equal to unity. Spanning each Z^2 region is a dashed line indicating the value of the middle-well potential peak. The first four exact levels are drawn in the center of each region, with odd and even levels drawn to the right and left of center, respectively. The first and second and the third and fourth levels have been connected via a line along the center to emphasize the level splitting. The case-1 and case-2 (lower energy) (for values of $Z^2\geq Z_c^2$) results are shown to the right and left of center, respectively, with all calculations done at the SUB(14,14) truncation. Odd and even levels are indicated via upward- and downward-pointing marks, respectively. All energy values are measured relative to the potential minima. A few results are off scale.

The absence of tunneling is also reflected in the excited-state CCM results built upon the shifted case-2 wave functions. It is particularly striking for the case of the deepest well, $Z^2=50$, shown. Here the energy of the first excited state *appears* numerically to have converged, but to a value which is very close to the average for the second nearly degenerate doublet, namely the second and third excited states. These plateaus of *quasiconvergence* seem to be typical of such calculations as the present CCM ones, which do not intrinsically include the major effects of tunneling from the outset. Presumably in this case, one would have to proceed to much higher levels of truncation for the first excitation energy to become unpinned from its quasiconverged value and actually converge to its exact value which is very nearly degenerate with that of the ground state.

For the CCM calculations based on the centered case-1 wave functions as zeroth-order approximants, we find a very accurate excitation spectrum around $Z^2=0$ (which corresponds to the pure quartic single-well limit). For values of $Z^2\lesssim 1$, the energy of the first excited state is well represented at the SUB(14,14) level. The same is true for the second and third excited states in the range $Z^2\lesssim 0.5$. We also note in passing that while the actual values of the energy levels are not so accurately reproduced at this level of approximation for deeper double-well potentials, the excitation spectrum that arises from use of the case-1 uncorrelated wave function does show some evidence of the splitting due to tunneling. We also remark that while the appearance of complex excitation energies in the calculated spectra is not explicitly indicated in Fig. 5, such complex values do occur for each of the calculations shown, except for the $Z^2=0$ and 0.5 case-1 and the $Z^2=50$ case-2 calculations.

It is clear that the double-well potentials provide the most severe test of all of the anharmonic potentials considered, for both the ground- and excited-state formalisms of the CCM as formulated and implemented here. With the exception of an inadequate description of phenomena connected with tunneling between the two wells, the method does, however, continue to produce results of high quality. This inability to describe tunneling accurately, at least at a reasonably low level of approximation, remains the most serious fault of the current implementation of the CCM approach. It seems clear that the basic cause of the problem is the use of a single uncorrelated state as the zeroth-order approximant. A multistate approach that simultaneously utilized, for example, both of the parity doublets that arise in the case-2 variational results, would almost certainly lead to much better results in this respect. We return to this point in our concluding remarks in Sec. IV.

IV. SUMMARY AND DISCUSSION

One of our main aims in this paper has been to present a detailed numerical analysis of the applicability of the CCM in situations where the initial zeroth-order wave function is not necessarily very close to the exact one. To this end we have chosen as our testing ground the model Hamiltonian of Eq. (2.1), which describes a rather general class of one-dimensional, one-body anharmonic oscillators. By choosing different combinations of values for the three coupling parameters ϵ, γ, and λ, it has been possible to produce models which make widely differing sets of demands on the CCM.

We presented initially a detailed study of the Hartree approximation for the ground-state wave function, which was later chosen as the starting or zeroth-order approximation for the CCM. The Hartree approximation may itself be defined in terms of a Bogoliubov-transformed harmonic oscillator ground state, chosen so as to minimize the energy expectation value, and with the transformation restricted to be unitary and to involve only real translations and rotations in the original oscillator phase space. The Hartree approximation was shown to be quite accurate in reproducing the ground-state energy for both the symmetric, pure quartic, and the asymmetric, equally weighted combination of cubic and quartic anharmonic oscillators, for a wide variety of coupling constants in each case. A rather severe and particularly interesting test of the Hartree approximation was posed by the symmetric, quartic double-well anharmonic oscillator. In this latter case we discussed in detail the various solutions that could arise. In particular, we observed a solution symmetric about the origin, which was seen to produce the lowest energy for shallow wells. Conversely, for sufficiently deep double wells, we also observed the possibilities of pairs of asymmetric solutions, shifted towards either of the two wells. For deep enough wells, these degenerate parity-doublet solutions produce the lowest energies in the Hartree approximation. Furthermore, they become asymptotically exact in the infinite-coupling limit in this case.

In the double-well case we observed, however, that there is a large region of intermediate values of the coupling constant where no single Hartree solution produces an accurate ground-state energy. This region coincides with the region where quantum tunneling between the two wells is of particular importance. We concluded the discussion in Sec. II on the variational estimates with a calculation of the ground and first excited states and the level splitting between them, which is based on linear combinations of the shifted (degenerate parity-doublet) Hartree states. We thereby obtained a very considerable improvement in the ground-state energies, especially in the intermediate regime.

The CCM was then described in some detail both for a description of the ground state and its energy eigenvalue, and for the excited states and their corresponding excitation energies. The SUB(m,n) truncation scheme was defined in order to effect a practical realization of the method, which may be systematically improved upon, in principle, by increasing the truncation indices m and n. These indices refer, respectively, to the degree of correlations built into the CCM excited and ground states with respect to the starting or zeroth-order wave function, which is now chosen as our previously obtained Hartree wave function. Finally, the CCM was applied to each of the three earlier benchmark models in turn.

The method was seen to produce extremely accurate ground-state energies for both the (symmetric) quartic and (asymmetric) cubic-plus-quartic anharmonicities. For all coupling constants in these two cases, we observed an extremely rapid initial convergence, followed by much slower convergence with oscillatory behavior about the exact result. Even for the cubic-plus-quartic case with coupling constant $\lambda=100$, which has about the largest error ($\sim 5\%$) for the ground-state energy in Hartree approximation, a CCM ground-state SUB(8) approximation decreases this error by a factor of better than 500. On the other hand, by proceeding to a much lengthier SUB(20) calculation, we obtain a further improvement by a factor of only about 5. We especially note that for practical implementations of the CCM to more realistic field-theoretical models of interest, it is the rapid initial convergence which is particularly encouraging, since one is most unlikely in such cases to be able to proceed beyond the few lowest levels of approximation.

In the case of the double-well potential, the CCM again gave a considerable improvement over the Hartree approximation, using the centered solution for shallow wells and the shifted solution for deep wells. However, for intermediate-depth wells, where quantum tunneling strongly influences the ground-state energy, neither Hartree starting point is satisfactorily improved via the CCM. It seems clear indeed that no description can be expected to work here which fails to take tunneling into account at some reasonably low level of approximation. It is probable that this is best achieved by including it, at least roughly, but essentially, in zeroth order. We return to this point in our concluding remarks.

We saw how the excitation spectrum was described by our CCM implementation of the Emrich parametrization for excited states, via the solution of a non-Hermitian eigenvalue problem. The method worked very well for the quartic anharmonic oscillator, even for very large anharmonicities, apart from the expected decrease in accuracy for the higher excited states. The situation is generally similar for the cubic-plus-quartic perturbation, although we now face the additional problem that since the higher levels are effectively sampling the more asymmetric regions of the potential, the accuracy is somewhat decreased. For the double-well potential, the problems observed in the ground-state calculations are echoed in the excitation spectrum. Thus, for very deep wells, the very small splitting of the first several pairs of nearly degenerate levels is not observed at all. Instead, the CCM excitation spectrum much more closely resembles what one would obtain in a potential where one of the two wells was totally removed.

Because the CCM eigenvalue problem of Eq. (3.16) for the excitation energies is not Hermitian, we are not guaranteed real energies *a priori*. One only knows that the description becomes exact in principle as both of the truncation indices m and n become infinite. Our expectation is that, since we are solving directly for the excitation energies, if the CCM description of both the ground and excited states is good, accurate and real values should result. Our results seem to confirm this view, with complex energies generally only appearing for large values of the excited-state truncation index m, and then only for the higher excited states. Furthermore, the problem becomes worse as the strength of the anharmonicity is increased. We have also seen some evidence, from the cubic-plus-quartic anharmonic oscillator data, that errors in the ground-state description are more important in this regard than those in the excited-state description.

We should also remind ourselves that it would be quite simple in the present case to avoid the problem of complex energies by working directly with the excited-state Schrödinger equation (3.11) and its CCM parametrization of Eq. (3.12). It is only by combining these equations with the ground-state equation to arrive at Eqs. (3.15) and (3.16), which directly yield the excitation energies rather than the absolute energies of the excited states, that the non-Hermiticity has arisen. In the present application of the CCM to the one-body problems considered here, a direct application of Eqs. (3.11) and (3.12) by projecting Eq. (3.11) onto the states $\langle \phi \mid b^n \exp(-\hat{S})$, would be perfectly possible. However, the method implemented here has two features which become very important in applications to many-body systems. Since one of our primary concerns here is to test the CCM on the simpler applications to anharmonic oscillators, we have therefore chosen to implement the CCM in the standard many-body fashion.

In the first place, by calculating the excitation energies directly we avoid complications connected with the inherent loss of accuracy associated with the almost complete cancellations between two nearly identical large numbers. Thus the ground-state energy of a system of N particles is a macroscopic variable which will scale like some power, N^{α}, of the particle number (where, for example, $\alpha=1$ for a self-bound, homogeneous system in equilibrium at finite saturation density), whereas the excitation energies of the low-lying states of particular interest are likely to be truly microscopic variables (i.e., of order one in comparison with N). This is true both for the low-lying single- and few-particle excited states and for the most important collective excitations. Secondly, the calculation of the excited states, as done here, utilizes much of the same information as that for the ground state. This can also be of considerable importance in a large-scale computation. We stress again that neither of these concerns is strictly relevant to the present application to the one-body problems studied here. Even so, we regard the non-Hermitian nature of the excited-state approximation as an intrinsic internal check on the accuracy of the method. We have seen that the pattern of the appearance of complex excitation energy eigenvalues generally encourages us to believe that at least the few lowest excited states are accurately represented.

We return finally to the question of the nonuniqueness of the solutions for the set of ground-state correlation amplitudes $\{S_i\}$, which arise from the coupled set of multinomial equations (3.10) at a given SUB(n) level of truncation. For a given truncation index n, these equations have a multiplicity of solutions, although it is not possible to enumerate the number of them once we restrict ourselves to real solutions as we have required from the outset. We have discussed in Sec. III A the numerical method of solution that we have adopted to obtain the solutions for the data presented. We refer to the solutions so found as the "standard" solutions. We reiterate how robust these normal solutions are to variations in the numerical procedures, and conversely how remarkably difficult it is to find any other "nonstandard" solutions out of the large number possible in principle for even only moderate values of the truncation index n.

Without making a very detailed study, we have, however, obtained and studied a few such nonstandard solutions by choosing different starting points for the hybrid Powell method. These alternate starting points were generated by straightforward iteration of Eq. (3.10) as in the standard method 2 of solution but *not* choosing the real root of smallest magnitude wherever possible, as was done previously. Frequently, these alternative starting points will still converge to the standard solution when inserted into the hybrid Powell scheme previously referred to as method 1. Occasionally, however, one does find a different, "nonstandard" solution. When they are found, convergence is usually much more difficult to achieve, and the resultant values of the ground-state and excitation energies are generally less accurate, by comparison with exact results, than the comparable ones obtained with the corresponding standard solution.

As an illustration of a case where convergence can be achieved, by our iterative method of solution, for a nonstandard solution, we present results for the quartic anharmonic oscillator with coupling constant $\lambda=0.1$. For this example we have found a nonstandard ground-state solution in the SUB(18) approximation which has an energy of 0.5589, and hence an error of about 0.03% compared to the exact result of 0.559 15. Although the corresponding standard solution is more accurate still by several orders of magnitude at the same truncation level, the nonstandard solution is clearly also rather accurate. Furthermore, when the nonstandard ground-state solution is used as input to a SUB(18,18) calculation of the excited states, the energies of the first four excited states are again quite well reproduced, with errors, respectively, of 0.52%, 0.56%, 1.00%, and 2.69%, although many of the higher levels in this approximation have complex energies. The standard solution again has much smaller corresponding errors, as may be seen from Table VI.

We show in Table X the corresponding solution $\{S_i\}$ for this model in order to contrast the standard and nonstandard ground-state solutions. We clearly observe that the two solutions are entirely different, particularly with respect to the relative magnitudes of the higher-order correlation coefficients. Even the lower-order coefficients are quite different, often being of opposite sign. It is particularly interesting to observe the quite different values for S_2 and S_4, although the two corresponding estimates for the energy, which as calculated via Eq. (3.9) depend only on S_2^2 and S_4, agree to about 0.03%.

It seems quite clear that at least at a given SUB(n) level of truncation the CCM is quite capable of producing more than one ground-state wave function (and hence, also, a corresponding spectrum of excited states), each of which gives the same energy eigenvalue. In principle the number of these nonstandard solutions grows as the truncation index n increases. It is not possible on the basis of the information presented here to make very authoritative statements about the convergence properties of any of these wave functions as $n \rightarrow \infty$. A discussion of this point would lead us too far astray from our main themes. However, it is quite possible that the CCM could produce a whole class of permissible ground-state wave functions for a given Hamiltonian in this $n \rightarrow \infty$ limit, with each having the same energy eigenvalue, since we are in principle working in a much enlarged CCM space of admissible wavefunctions than the usual Hilbert space of normalizable wave functions. Thus our entire CCM program, and in particular the method of calculating the ground-state energy, $E = \langle \phi | H | \psi \rangle / \langle \phi | \psi \rangle$ as the projection of the Schrödinger equation (3.4) with the model state $\langle \phi |$, [or, equivalently, $E = \langle \phi | He^S | \phi \rangle / \langle \phi | \phi \rangle$ as in Eq. (3.5)], never requires the state $| \psi \rangle$ to be normalizable. We can contrast this with the more usual method of calculating the energy as $E = \langle \psi | H | \psi \rangle / \langle \psi | \psi \rangle$. Our only requirement has been that the model state $| \phi \rangle$ is normalizable and that the overlap $\langle \phi | \psi \rangle$ is nonzero and finite (and actually equal to $\langle \phi | \phi \rangle$ by chosen construction).

We note also that none of the truncated CCM wave functions is normalizable in *any* finite SUB(n) approximation with $n > 2$. If the approximations do converge in some meaningful fashion as $n \rightarrow \infty$, it is clear that only one of the possible multiple solutions will become the usual normalizable wave function, and it is probable that this solution will be our previous "standard" solution. Furthermore, it seems most likely that, in this case, the remaining "nonstandard" solutions will converge to different solutions $| \psi \rangle$ which, although nonnormalizable, will all have the same energy eigenvalue when calculated via Eq. (3.5). Whether these nonstandard solutions or, equivalently, our CCM enlargement of the usual Hilbert space for quantum mechanics, are simply curiosities or are potentially useful, must await their further study that we intend to perform.

TABLE X. Comparison of the ground-state correlation coefficients $\{S_i\}$ for SUB(18), $\lambda = 0.1$, for the quartic anharmonic oscillator, calculated via the standard method and for one of the nonstandard root choices.

	S_i	
i	Standard	Nonstandard
2	1.5974×10^{-3}	-1.7514×10^{-3}
4	-2.8871×10^{-3}	-2.4485×10^{-3}
6	7.4128×10^{-5}	1.4157×10^{-4}
8	-2.6550×10^{-6}	-4.6374×10^{-4}
10	1.0950×10^{-7}	-3.9578×10^{-5}
12	-4.8976×10^{-9}	4.1194×10^{-5}
14	2.3219×10^{-10}	-6.1199×10^{-6}
16	-1.0759×10^{-11}	-2.1472×10^{-7}
18	3.5769×10^{-13}	1.1916×10^{-7}

In summary, by applying the CCM to various classes of one-body anharmonic oscillator Hamiltonians, we have found the method to be very resilient to inaccuracies in the starting wave function of zeroth order. The only real problem concerned the double-well potential, where an intrinsic description of tunneling was seen to be absent from our CCM prescription built on a single zeroth-order model (or reference) state. In this respect, it is likely that one needs to extend our CCM prescription to one built on a multireference state approach. This is clearly indicated even at the Hartree level by the results of our Sec. II E. We note that there exist several variants of coupled-cluster theory employing a multireference state approach.[11,26–29] These have largely been developed with open-shell systems in mind, both for atomic nuclei[26,27] and for many-electron systems in quantum chemistry.[11,28,29] Unfortunately, non of these variants seems immediately applicable to our present needs, as we discuss more fully below.

We note that the general topic illustrated in the present paper by applications to the model Hamiltonian systems of anharmonic oscillators should also be of particular topical interest in such areas as quantum chemistry, where the CCM has become widely applied. For example, applications to molecular systems of both the Emrich approach considered here and the (multireference-state) open-shell approach referred to previously are currently being performed by several groups. In this context, such quantities as excitation energies, ionization potentials, and electron affinities are probably of most interest. A new generation of coupled-cluster calculations has been initiated for these quantities, which may then be compared with the results from such older techniques as, for example, the Hartree-Fock, configuration-interaction (CI),[30] and Green's-function methods. The interested reader is referred to the recent literature for further details of these quantum chemistry applications. Refs. 12 and 31–35 are an illustrative, but by no means exhaustive, selection of the current work in this area.

One of the very great advantages of the CCM over, for example, the CI method, is its size-extensivity property. Thus for a many-body theory to be able to be applied over a wide range of particle numbers, and to be numerically stable, it must be size extensive in the sense of generating values for such extensive variables as the energy, which scale correctly with particle number. For example, the CI method contains disconnected diagrams for the energy and suffers accordingly from the so-called size-extensivity or size-consistency problem.[7,36,37] As is well known,[7] the ground-state CCM based on a single reference state, as discussed in Sec. III, resolves this problem and contains no disconnected energy diagrams. The same is also true for the straightforward Emrich extension of this formalism to excited states, which we have similarly discussed in Sec. III and employed in the present work. Indeed, one of the particular attractions of this excited-state formalism is that the spectrum is given directly in the form of excitation energies, rather than having to take the differences of absolute excited-state and ground-state energy eigenvalues.

By contrast, in the extension of the CCM to a multireference state approach,[11,26,29] the size-extensivity problem is not necessarily trivial to satisfy in practical applications. In this approach, one chooses some set of (quasidegenerate) reference states (e.g., Slater determinants for many-fermion systems, built from single-particle orbitals which include a set of valence orbitals), which approximately span the desired set of eigenfunctions. Typically, one then constructs some effective Hamiltonian that acts on only a small subset of all possible reference states (the so-called model space), but in such a way that it exactly reproduces some selected portion (typically the lowest portion) of the eigenspectrum of the full Hamiltonian in the full space.

In order to satisfy the size-extensivity property, it is sufficient to ensure that this effective Hamiltonian contains only connected terms. Until relatively recently this was thought to imply that the model space should be *complete* in the sense described below. An N-fermion model space is typically spanned by some set of N-particle Slater determinants. These determinantal states are constructed from a set of single-particle orbitals which typically are either labeled as *core* orbitals or *valence* orbitals. The core orbitals are, by definition, completely occupied in each determinantal state by N_c fermions. By contrast, the valence orbitals are only partially occupied by the remaining $N_v = (N - N_c)$ fermions. If the model space includes all determinants such that the N_v fermions are allocated to the valence orbitals in all possible ways, the model space is said to be complete. While such multireference state extensions of the CCM in complete model spaces retain the size-extensivity property, such complete spaces are often prohibitively large for practical calculations. Recent work[38,39] has shown how the size-extensivity property may also be retained in suitably defined incomplete model spaces. A discussion of this point would take us too far afield for present purposes, however, and the interested reader is referred to the literature[38,39] for further details.

It is not yet clear whether the Emrich approach to excited states considered here, or the multireference state approach employing an effective Hamiltonian amd model space, will ultimately be the more useful in practical applications to such fields as quantum chemistry. For truly extended (e.g., condensed-matter or field-theoretic) systems, the Emrich approach certainly seems more natural, since the division of single-particle states into core, valence, and unoccupied states would in such cases usually be very artificial. Conversely, for relatively small systems such as many atoms and molecules, the multireference state approach seems very physical.

We have already indicated that for applications to anharmonic oscillators with double-well or multiwell potentials, and to the comparable soliton-bearing field theories, an extension of the CCM appears to be necessary if one wishes particularly to describe the important consequences of quantum tunneling. What appears to be necessary here is some version of the CCM which incorporates both the underlying concepts of the Emrich formalism as well as a multireference state approach. However, none of the existing versions of the open-shell multireference state formalism as described in outline above, seems easily to adapt itself to the case where the multiple reference states differ not by small ("local") changes in the occupation of the valence orbitals, but rather by some global symmetry property. Thus, in the case of the double-well anharmonic oscillator, for example, we would like to employ the shifted parity doublets as a pair of reference states to be built into the starting-point of the CCM formalism on an equal footing. One may easily imagine that such a formalism could also be very useful in quantum chemistry, for example, for applications to molecules that exhibit analogous (broken) symmetry properties. We hope to return to this problem at a later stage.

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