Paths to optimization in the multistate Rayleigh-Ritz variational method: Applications to the double-well quantum anharmonic oscillator

R. F. Bishop and M. F. Flynn

*Department of Mathematics, University of Manchester Institute of Science and Technology,
P.O. Box 88, Manchester M60 1QD, England*

M. C. Boscá and R. Guardiola

Departamento de Física Moderna, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

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Both single-well and multiwell one-dimensional anharmonic oscillators have provided an extremely fruitful testing ground for various modern techniques of microscopic quantum many-body theory and quantum field theory. They have served both as $(0+1)$ -dimensional field-theory models of their important counterparts in a higher number of dimensions, and as algebraically simple yet highly nontrivial problems on which various approximation or truncation schemes could be tested to very high orders. Such techniques have included perturbation theory and its many possible resummation schemes, and the coupled-cluster method. In the present paper the spotlight is focused on variational methods, and we concentrate on their application to the particularly demanding double-well quartic anharmonic oscillator. We examine in detail both single-state and multi-state variational calculations based on either orthogonal (uncorrelated) or nonorthogonal (correlated) basis functions. Particular attention is paid to the question of the sensitivity and accuracy of the results with respect to any nonlinear parameters that characterize the basis states. Practical schemes are suggested for their choice and are shown to be capable of very high accuracy. Use of this simple model also allows detailed comparisons to be made with other techniques of a perturbative or perturbative-variational hybrid character.

I. INTRODUCTION

One of the most widely used and successful techniques for calculating the ground-state energy of a quantum system is the Rayleigh-Ritz variational method. As well as being both capable of high accuracy and relatively simple to implement, at least conceptually, it has the extremely valuable upper-boundedness property. Thus, so long as no further approximations are made, the estimate generated for the energy eigenvalue is guaranteed to be greater than (or equal to) the corresponding exact result. The method has been widely applied with enormous success and great accuracy to quantal systems ranging from the textbook examples for one-body problems to such few-body systems as the three- and four-nucleon systems ^3H and ^4He ,¹⁻⁹ systems of intermediate particle number such as the light nuclei ^{12}C and ^{16}O ,¹⁰⁻¹³ and the infinite many-body problem for both Bose and Fermi systems.¹⁴⁻²¹

A typical trial wave function of the simplest type will involve a single functional form. The shape of this function is generally chosen according to certain physical considerations of the specific system under consideration. It will also generally depend upon certain free parameters, which are themselves usually chosen so as to minimize the variational estimate of the energy. In order to distinguish such calculations from their extensions considered below, we shall refer to them generically as the single-state variational method (SSVM). Typical calculations of this sort for few-body systems, for example, in-

volve the use of correlated trial wave functions, $\psi = \hat{F}\phi$, where $\phi = \phi(1, 2, \dots, N)$ describes some independent-particle motion of the N -body system, and $\hat{F} = \hat{F}(1, 2, \dots, N)$ is a correlation operator. The uncorrelated wave function ϕ is usually chosen to reflect the underlying symmetry properties of the system, and to be a function of some suitable set of intrinsic coordinates, such as the well-known Jacobi coordinates in coordinate space. The purpose of the correlation operator $\hat{F}$ is to introduce dynamic correlations as far as is practicable. A standard calculation of this type^{1,2,4} would parametrize $\hat{F}$ in the well-known Jastrow form

$$\hat{F}(1, 2, \dots, N) = \prod_{i < j=1}^N f(|\mathbf{r}_i - \mathbf{r}_j|), \quad (1)$$

where the central correlation function $f(r)$ should satisfy such typical boundary conditions that it vanishes inside any hard-core radius of the two-body potential (or otherwise approach zero as r tends to zero, if the potential becomes infinite there), and approach unity as the separation distance r becomes large. Suitable parametric forms may then be chosen for the functions f and ϕ .

More sophisticated variants of this simple method have also been developed. For example, if the interparticle interaction contains such noncentral components as a tensor force, the simple (central) Jastrow wave function above usually gives rather poor bounds on the energy eigenvalue, since in this case the expectation value of the tensor operator $\hat{S}_{12}$ in such Jastrow correlated wave functions vanishes identically. To take such state dependence

into account, one needs to replace the correlation operator of Eq. (1) by a symmetrized product of pairwise correlation operators, which themselves contain both central and suitable noncentral pieces.⁶ The remaining integrals in effecting the Rayleigh-Ritz estimate for the energy then usually require Monte Carlo techniques for their evaluation.⁶ A somewhat simplified version of this (generalized) Jastrow method is the so-called ATMS (or amalgamation of two-body correlations into a multiple-scattering process) method of Akaishi *et al.*,⁵ which again includes noncentral correlations, but now only linearly as opposed to all orders.

What characterizes all such calculations is that they involve only a single or a few functions to specify the correlation operator and hence the trial wave function. Most realistic calculations parametrize these functions with preconceived functional forms based on physical intuition, and fix the few remaining parameters variationally. Although it is possible in principle to determine the actual form of the functions by a functional variation, via the solution of the resulting Euler-Lagrange integro-differential equations, such calculations are extremely complex and time consuming for most realistic systems. An alternative and rather successful way to extend the SSVM techniques is based upon an expansion of the trial wave function in a truncated subset of a complete set of basis functions. It is the resulting so-called multistate variational method (MSVM) that is the primary focus of attention of the present paper.

These MSVM techniques are based upon trial wave functions formed from a linear combination of a certain number J of linearly independent functions χ_j ,

$$\psi(1, 2, \dots, N) = \sum_{j=1}^J c_j \chi_j(1, 2, \dots, N). \quad (2)$$

Both the set of linear parameters $\{c_j\}$ and any nonlinear parameters contained within the basis function set $\{\chi_j\}$ are to be determined variationally by minimization of the resulting Rayleigh-Ritz estimate for the energy. It is then trivial to show that the linear parameters are thus determined by the diagonalization of the energy matrix within the truncated basis,

$$\sum_{j=1}^J (\langle \chi_i | H | \chi_j \rangle - E \langle \chi_i | \chi_j \rangle) c_j = 0, \quad i = 1, \dots, J. \quad (3)$$

The necessary and sufficient condition for this system of equations (3) to have a nontrivial solution is that the determinant of the coefficients vanish. According to a well-known theorem²² (variously known as the interlace or interlacing theorem, or the Hylleraas-Undheim theorem, among others names), the resulting ordered set of J roots for E provides upper bounds to the corresponding lowest J exact eigenvalues. Furthermore, the exact eigenvalues are approached monotonically as the dimension J of the basis is increased. Apart from the fact that the MSVM now gives variational estimates for an arbitrary number J of energy eigenvalues in comparison to just one (viz., the lowest) for the SSVM, this latter feature is the clearest advantage of the MSVM over most com-

parable attempts to generalize or improve the SSVM.

Practical calculations with the MSVM may again be performed with either uncorrelated or correlated basis functions. A typical few-body problem, such as the triton, has been analyzed⁷ in the former case using standard harmonic-oscillator basis functions referred to two intrinsic three-vector Jacobi coordinates. The main disadvantage of such calculations is that the energy estimates converge relatively slowly and the size of the basis needs to be correspondingly large. Furthermore, even when the energy convergence is well attained, one has no guarantee that other physical quantities are well represented. The underlying problem is that both the "correlation hole," due to dynamic correlations, within the exact wave function, and its correct asymptotic form now have to be constructed from a set of basis functions which neither contain any correlations nor share the same asymptotic behavior. Consequently, the basis size often needs to be prohibitively large. These disadvantages may be overcome by using correlated basis functions constructed from the previous uncorrelated (harmonic-oscillator) basis by means of a correlation operator analogous to the Jastrow form of Eq. (1). A typical example of the use of this method for the case of the triton is given in Ref. 8.

In using either the SSVM or the MSVM one still has to choose any free nonlinear parameters that are contained within the trial wave functions. Searches over a set of such parameters to locate the minimum energy estimate can be quite time consuming within the context of an MSVM calculation employing a large basis. In this light it is tempting to assume that at least approximately appropriate values of these parameters can be determined in a low-order calculation, say, the corresponding $J=1$ SSVM case, and then frozen at these values for use in the corresponding extended MSVM calculations. However, this procedure can turn out to be extremely inaccurate or misleading, especially when the individual basis functions themselves provide a rather poor description of the ground state of the interacting system. A typical situation has been examined by Balsa *et al.*²³ for the cases of the one-body single- and double-well quartic anharmonic oscillators, using as trial wave functions the complete orthogonal basis of harmonic-oscillator wave functions but with the oscillator constant as a free parameter. We note in passing that a similar extreme sensitivity of the results of perturbation theory in this case to the corresponding choice of unperturbed harmonic-oscillator Hamiltonian, with the same oscillator constant regarded as a free parameter, has been noted and exploited by Killingbeck²⁴ to achieve vastly improved perturbative results for these systems. We return to this point in our concluding remarks in Sec. IV.

In this paper we wish to reexamine critically and to extend considerably the work of Balsa *et al.* in order to shed as much light as possible on the points raised above, and in as wide a context as possible. The particular system that we will use as a testing ground to illustrate the main points is the one-body double-well quartic anharmonic oscillator in one dimension, with the Hamiltonian given in terms of the position coordinate x and canonically conjugate momentum $p \equiv -i\hbar/dx$, as

$$H_2 = \frac{1}{2}p^2 + \frac{1}{2}(x^2 - \frac{1}{2}Z^2)^2. \quad (4)$$

This problem is treated in Sec. II by the MSVM in its simplest manifestation, namely, where the basis states form a complete orthogonal set. For this case we use the standard harmonic-oscillator states, and treat the oscillator parameter as our sole free nonlinear variational parameter. We show that the sensitivity to this parameter is quite strong, and that the way of fixing it suggested by Balsa *et al.* is far from being optimal in practice.

While the above basis states have the advantage of simplicity due to their orthogonality, they provide an extremely bad approximation to the exact ground state of the double-well Hamiltonian of Eq. (4), especially for large values of the parameter Z^2 which determines the height of the barrier between the wells. In such cases a more natural SSVM calculation for the ground-state energy might consider a linear combination of two Gaussian (i.e., ground-state harmonic-oscillator) wave functions centered around the bottom of each well. We show in Sec. III that such a SSVM calculation with a good starting wave function can also be rather easily generalized to its MSVM counterpart. One way to do this is to use the above single trial wave function as the seed or initial function on which to construct a Lanczos-like basis²⁵ of linearly independent trial states by repeated action upon it with the Hamiltonian operator of Eq. (4). This method involving nonorthogonal correlated basis functions is discussed in Sec. III, and the results of it are compared and contrasted with the corresponding ones using the uncorrelated orthogonal basis.

Finally, the general features of the results are discussed in Sec. IV. Comparisons with other related methods are made, and possible implications of our results are explored.

II. THE MSVM IN AN ORTHOGONAL BASIS

As we have already seen, the MSVM in an orthogonal basis $\{\chi_n\}$ is equivalent to diagonalization of the truncated Hamiltonian matrix. Upper bounds for the lowest N eigenvalues are obtained from the solution to the polynomial equation

$$\det(\langle \chi_m | H | \chi_n \rangle - E \delta_{mn}) = 0, \quad m, n = 0, 1, \dots, (N-1). \quad (5)$$

For the case of the one-dimensional quartic anharmonic oscillators, Balsa *et al.*²³ have studied the MSVM within the rather natural orthogonal basis for $-\infty < x < \infty$:

$$\chi_n(x) = (2^n n! \pi^{1/2} \alpha^{-1})^{-1/2} H_n(\alpha x) \exp(-\frac{1}{2} \alpha^2 x^2), \quad n = 0, 1, 2, \dots, \quad (6)$$

in terms of the standard Hermite polynomials $H_n(z)$, appropriate to an "unperturbed" Hamiltonian

$$H_0 = \frac{1}{2}p^2 + \frac{1}{2}\alpha^4 x^2, \quad (7)$$

corresponding to a harmonic oscillator with unspecified parameter α^2 . For the corresponding SSVM in this case it is natural to choose χ_0 as the trial wave function, and

to determine α^2 by minimizing the corresponding variational estimate $\epsilon_0 \equiv \langle \chi_0 | H | \chi_0 \rangle$ of the exact ground-state energy E_0 , with respect to the parameter α^2 :

$$d\epsilon_0/d\alpha^2 = 0. \quad (8)$$

For the case of the single-well quartic anharmonic oscillator with Hamiltonian,

$$H_1 = \frac{1}{2}p^2 + \frac{1}{2}x^2 + \lambda x^4, \quad \lambda > 0 \quad (9)$$

it is easily shown that ϵ_0 is given as

$$\epsilon_0(\alpha) \equiv \langle \chi_0 | H_1 | \chi_0 \rangle = \frac{1}{4} \left[\alpha^2 + \frac{1}{\alpha^2} \right] + \frac{3\lambda}{4\alpha^4}. \quad (10)$$

The condition of Eq. (8) then gives explicitly

$$\alpha^6 - \alpha^2 - 6\lambda = 0. \quad (11)$$

Considered as a cubic equation in α^2 , Eq. (11) has exactly one real positive solution $\alpha^2 = \bar{\alpha}^2 > 0$ for each $\lambda > 0$. It has been observed elsewhere²⁶ that the corresponding minimized value of ϵ_0 , namely,

$$\bar{\epsilon}_0 = \epsilon_0(\bar{\alpha}^2) = \frac{3\bar{\alpha}^4 + 1}{8\bar{\alpha}^2}, \quad (12)$$

gives a variational estimate for the ground-state energy which is accurate to better than about 2% for *all* (positive) values of the anharmonic coupling constant λ . Balsa *et al.*²³ have shown that using the same value $\alpha = \bar{\alpha}$ in the MSVM as determined by the SSVM described here now leads to a rapidly convergent set of approximations for the energies of the excited states as well as for the ground state, as a function of basis size N .

If the same procedure is now adopted for the symmetric double-well Hamiltonian H_2 of Eq. (4), the situation is very different. If we again use $\chi_0(x)$ as the trial wave function in a SSVM approach, the corresponding estimate for the ground-state energy becomes increasingly bad as the parameter Z^2 is increased. Thus for $Z^2 = 0$ the optimal error in the exact ground-state energy after minimization of the corresponding expression for $\epsilon_0 \equiv \langle \chi_0 | H_2 | \chi_0 \rangle$ as a function of α^2 is about 2%. The corresponding respective errors for $Z^2 = 1, 2$, and 3 have increased to approximately 5%, 10%, and 17.5%. It is clear that as Z^2 increases even further the depth of the two symmetric wells continues to increase and the trial wave function $\chi_0(x)$ becomes increasingly bad. As a measure of the depth $V_p \equiv Z^4/8$ of the mid-well peak between the maximum at $x=0$ and the two minima at $x = \pm 2^{-1/2}|Z|$, we note that the ratios E_0/V_p take the values 3.63, 1.14, and 0.74 for the respective values of $Z^2 = 1, 2$, and 3. As Z^2 increases, the lowest levels E_0 and E_1 become increasingly close to each other due to the diminishing probability of quantum tunneling between the two wells as the ratio E_0/V_p becomes appreciably less than 1.

For values $Z^2 \gtrsim 3$, it seems clear that a better orthogonal set of trial wave functions would be the comparable harmonic-oscillator basis to Eq. (6) but now translationally shifted to be centered around either $x = |x_0|$ or

$x = -|x_0|$, where $|x_0|$ is another free parameter which is expected to approach $2^{-1/2}|Z|$ as Z^2 increases. That this is indeed the case has been discussed quantitatively elsewhere.²⁶ For example, such a ground-state shifted oscillator trial wave function, when optimized with respect to both x_0 and α^2 , gives errors for the ground-state energy for $Z^2=4, 5, 10$, and 50 of approximately 14%, 5%, 0.6%, and 0.04%, respectively. It is clear that an even better basis, particularly to resolve the splitting of the narrowly spaced parity doublets as Z^2 becomes large, would involve the *simultaneous* use of the two (otherwise equivalent) translationally shifted harmonic oscillator bases. We defer further discussion of this point until Sec. III.

In the meantime, we return to the unshifted basis of Eq. (6), and consider first an alternative suggestion of Balsa *et al.*²³ to improve the convergence properties of the MSVM approach for the double-well Hamiltonian H_2 of Eq. (4) using this basis. These authors have pointed out the rather obvious feature that, unlike the case of the single-well anharmonic oscillator of Eq. (9), the state $\chi_0(x)$ is no longer obviously the best single choice of a SSVM trial wave function out of the basis set $\{\chi_n(x)\}$ of Eq. (6), since for $n > 0$ the “unperturbed” probability density $\chi_n^2(x)$ for finding the particle at a given position x is maximal at some nonzero value of x^2 . Such considerations led them to increase the variational space by choosing $\epsilon_0(\alpha^2, n) \equiv \langle \chi_n | H_2 | \chi_n \rangle$ as their SSVM estimate for the ground-state energy, which they then minimize with respect to both α^2 and n . Using the explicit form of the double-well Hamiltonian from Eq. (4) it is easy to show that

$$\epsilon_0(\alpha^2, n) \equiv \langle \chi_n | H_2 | \chi_n \rangle = \frac{Z^4}{8} + \frac{1}{2}(n + \frac{1}{2}) \left[\alpha^2 - \frac{Z^2}{\alpha^2} \right] + \frac{3}{8\alpha^4}(2n^2 + 2n + 1). \quad (13)$$

Minimization of Eq. (13) with respect to α^2 and n leads respectively to the two equations

$$\alpha^6 + Z^2\alpha^2 - \frac{3(2n^2 + 2n + 1)}{(2n + 1)} = 0 \quad (14)$$

and

$$\alpha^6 - Z^2\alpha^2 + 3(n + \frac{1}{2}) = 0. \quad (15)$$

Elimination of the variable n between Eqs. (14) and (15) trivially yields the relation which produces the optimal value of Balsa *et al.* for α^2 as

$$\alpha^{12} - Z^2\alpha^8 + \frac{9}{8} = 0. \quad (16)$$

For large values of Z^2 a very good approximate solution to one of the roots of Eq. (16) is $\alpha^2 = |Z|$. Their corresponding optimal value for n is then obtained from either of Eqs. (14) or (15).

In practice, Balsa *et al.* have then used the same approximate value $\alpha^2 = |Z|$ in the corresponding MSVM calculations using bases of varying size N . They have demonstrated that the convergence for large values of $|Z|$

to accurate estimates of the energy eigenvalues for the Hamiltonian of Eq. (4), is much faster as a function of basis size N using this (fixed) value of the parameter α^2 , rather than using that value determined by minimization of $\epsilon_0 = \langle \chi_0 | H_2 | \chi_0 \rangle$ as in Eq. (8). It is clear from this observation that the extra degree of freedom allowed by the introduction of the parameter n as an additional variational parameter is important. However, it is clear by inspection of Eqs. (14) and (15) that their approximate root $\alpha^2 \approx |Z|$ is combined with a corresponding value of $n + \frac{1}{2} \approx 3/8|Z|^3$. Thus, although the original rationale for introducing higher harmonic-oscillator wave functions as candidates for the SSVM trial function remains valid, the particular solution $\alpha^2 \approx |Z|$ used by Balsa *et al.* is only actually consistent with the original choice $n=0$.

The above anomaly in their method has led us firstly to modify their criterion for the choice of the SSVM parameters, and secondly to consider more widely the dependence of the corresponding MSVM calculations on this choice. Thus in the first place we shall adopt the simple criterion of optimizing the SSVM value of α^2 for a given value of n by solving Eq. (14). This unique real root $\alpha^2 = \bar{\alpha}^2(n)$ is then furthermore used in the corresponding MSVM calculation with a basis of size $N = n + 1$. It is clear that other choices are possible and we shall return later to the question of the sensitivity of the accuracy of the results to the choice for the parameter α^2 . For the moment we simply note that our choice has the twin virtues of simplicity and of reducing to the standard SSVM choice in the $n=0$ limit. For actual numerical computations we also note that since parity is a good quantum number for the eigenstates of the Hamiltonian of Eq. (4), the even and odd states can be obtained by completely separate diagonalizations. For example, estimates for the energies of the lowest M even states are obtained within the MSVM by using the lowest M even trial wave functions $\{\chi_n, n=0, 2, \dots, 2M-2\}$. The parameter α^2 is chosen by solving Eq. (14) with $n=2M-2$. The odd states are handled similarly.

In Table I we compare the corresponding results obtained via the criterion $\alpha^2 = |Z|$ of Balsa *et al.* and via the present method, for the deep double-well potential of Eq. (4) with $Z^2=50$. In particular, we give typical results for the zeroth and 38th states obtained from using even trial wave functions only, and for the first and 39th states obtained from using odd trial wave functions only. It should be noted that for ease of comparison both the even and odd states determined using our criterion and by separate diagonalizations of the matrices of a given $(M \times M)$ order are found with the same value of $\alpha^2 = \bar{\alpha}^2(2M-2)$ obtained for the even states. That is, the results from the M th-order MSVM for the odd states displayed in Table I use the *same* value of α^2 as that obtained from the optimized M th-order MSVM for the even states, using our new criterion.

In view of our earlier discussion it is perhaps not surprising that the results displayed show that our new criterion is considerably more effective at exploiting the extra flexibility afforded by the introduction of the index n as an extra variational parameter, than the earlier criterion of Balsa *et al.* For the ground-state energy E_0 , for

TABLE I. Values of the MSVM energies of the ground state, and the first, 38th, and 39th excited states for the deep double-well quartic-anharmonic-oscillator potential of Eq. (4) with $Z^2=50$, as a function of order M of implementation and using the orthogonal harmonic-oscillator basis of Eq. (6). The BPEP values use the value $\alpha^2=|Z|$ of Ref. 23, while the present method uses the order-dependent α^2 value from Eq. (14) with $n=2M-2$.

M	BPEP method		α^2	Present method	
	E_0/E_1	E_{38}/E_{39}		E_0/E_1	E_{38}/E_{39}
1	312.507 500 000		0.059 995 680 9	208.348 332 793	
	312.537 500 000		0.059 995 680 9	208.408 328 473	
10	228.857 248 661		0.567 915 572 8	8.859 927 521	
	223.806 800 533		0.567 915 572 8	8.364 847 896	
20	136.624 606 117	530.944 571 761	1.141 055 937	5.037 280 168	567.110 592 768
	132.586 667 891	537.419 083 732	1.141 055 937	5.044 195 744	621.885 994 353
30	67.780 986 993	368.149 601 281	1.676 300 880	4.990 015 387	276.881 099 043
	65.015 609 317	371.954 484 749	1.676 300 880	4.990 010 765	271.399 581 821
40	24.943 902 936	314.571 202 582	2.166 890 709 1	4.989 954 561	213.766 610 789
	23.484 634 519	315.771 119 578	2.166 890 709 1	4.989 954 554	210.509 137 688
50	7.076 529 326	279.108 389 845	2.613 343 204 6	4.989 954 548	187.145 654 479
	6.736 569 102	276.960 576 330	2.613 343 204 6	4.989 954 548	185.836 575 738
60	4.993 580 719	236.576 860 010	3.019 599 225 3	4.989 954 548	181.987 382 014
	4.992 113 091	234.560 010 813	3.019 599 225 3	4.989 954 548	181.972 444 406
70	4.989 954 549	200.814 610 530	3.390 622 286 1	4.989 954 548	181.943 610 338
	4.989 954 548	199.353 830 049	3.390 622 286 1	4.989 954 548	181.943 612 813
80	4.989 954 548	182.269 093 441	3.731 245 925 5	4.989 954 548	181.943 599 502
	4.989 954 548	182.122 905 392	3.731 245 925 5	4.989 954 548	181.943 599 502
90	4.989 954 548	181.943 599 533	4.045 746 643 7	4.989 954 548	181.943 599 501
	4.989 954 548	181.943 599 515	4.045 746 643 7	4.989 954 548	181.943 599 501
100	4.989 954 548	181.943 599 501	4.337 755 712 5	4.989 954 548	181.943 599 501
	4.989 954 548	181.943 599 501	4.337 755 712 5	4.989 954 548	181.943 599 501

example, an accuracy of ten significant figures is now achieved with a basis size of under 50, as opposed to the basis size of approximately 70 that is required by the previous criterion. If one is satisfied with lower accuracy, the difference is even more striking. Thus 1% accuracy is achieved for E_0 with a basis size $M=20$ by our new criterion, whereas by the previous criterion such accuracy is not achieved until the basis size is at least 57. Similar comparisons also hold for other energy levels.

The differences between the two choices of α^2 may also be rather strikingly seen from Fig. 1, where we display the accuracy of the ground-state energy as a function of α^2 for various values of the number M of harmonic-oscillator trial wave functions used in the MSVM. Results are again given for the case $Z^2=50$ of a deep double-well potential. One observes quite clearly that our very simple prescription for choosing α^2 at a given value of the basis size M , gives values which are very close to the optimal values. It is also apparent that the energy attainable at a given order (i.e., at a given basis size) in the MSVM is strongly dependent upon α^2 , and that the optimal values do depend appreciably upon M . Although, conversely, the approximate value $\alpha^2 \approx |Z|$ of Balsa *et al.* is in general far from the optimal value, it is nevertheless usually still a distinct improvement over the value of α^2 provided by the usual ground-state SSVM criterion of Eq. (8), as these authors originally claimed.²³ Figure 1

FIG. 1. Accuracy, as a function of the nonlinear variational parameter α^2 , of the ground-state energy E_0 for the deep double-well quartic-anharmonic-oscillator potential with $Z^2=50$, as calculated in the MSVM using the orthogonal harmonic basis of Eq. (6) and at various orders M of implementation, namely, $M=20$ (solid line), 40 (dashed line), 60 (dotted line), 80 (dashed-dotted line), and 100 (dashed-double dotted line). Accuracy, defined as $-\log_{10}(E_0/E_0^{\text{exact}} - 1)$, is a measure of the number of significant figures. The points marked on the curves indicate the approximately optimal values of α^2 as determined by the present order-dependent criterion discussed in the text.

demonstrates that the criterion of Balsa *et al.* really only becomes at all useful for basis sizes greater than about 60. Even then, our own choice usually gives much greater accuracy.

III. THE MSVM IN A NONORTHOGONAL BASIS

It seems likely that the extreme sensitivity to the choice of the nonlinear parameter α^2 in the trial functions in the MSVM that we have observed in Sec. II is a consequence of the fact that the orthogonal basis used is rather inappropriate to the deep double-well potential considered. Indeed, if we continue to restrict ourselves to orthogonal basis sets, it is difficult to see how to improve this situation easily. While we might readily use the same harmonic-oscillator wave functions as in Eq. (6), but now with the origin shifted by an amount $\pm b$ towards the location of the minimum of either one of the two wells, and furthermore then use the parameter b as an additional variational parameter, this by itself is unlikely to improve the situation dramatically. Thus neither of these two

shifted orthogonal sets has parity as a good quantum number, and hence the even and odd states can no longer be separately considered. The consequent problem is then that for deep double wells it is physically obvious that a large number of states in such a shifted basis would need to be sampled in order to describe accurately the very small splitting of the almost degenerate low-lying parity doublets in the exact energy spectrum.

One remedy to the above problem would be to use as the MSVM trial states the parity-conserving combinations $\{\chi_n^{(\pm)}(x)\}$ for the even and odd states separately, where

$$\chi_n^{(\pm)}(x) \equiv \chi_n(x+b) \pm \chi_n(x-b). \quad (17)$$

We are thus led rather naturally to consider nonorthogonal basis sets within the MSVM as a possible means of decreasing the sensitivity to the inbuilt nonlinear parameters and of increasing the accuracy at a given order of implementation (i.e., for a given number of linearly independent trial functions). For present illustrative purposes we prefer not to use the nonorthogonal sets $\{\chi_n^{(\pm)}\}$ of Eq. (17), since they still rely on the underlying orthogonal

TABLE II. Values for the MSVM energies of the lowest four even states of the double-well quartic-anharmonic-oscillator potential of Eq. (4) for various values of Z^2 and at various orders N of the implementation, using the nonorthogonal moment-generating basis of Eq. (18) with the single-Gaussian seed-generating function $\chi_0(x)$. For each level the variational parameter α^2 is chosen to minimize its particular energy estimate at order $N=9$. The results marked E in the N (order) column are exact.

Z^2	N	E_0	E_2	E_4	E_6
0	1	0.737 086 8			
	2	0.556 474 5	4.606 219 3		
	3	0.532 748 4	3.871 788 5	9.828 923 7	
	4	0.530 371 2	3.745 157 9	8.480 942 9	15.996 224 9
	5	0.530 193 0	3.729 414 2	8.186 136 8	13.959 575 0
	6	0.530 181 7	3.727 963 6	8.137 162 4	13.398 815 0
	7	0.530 181 1	3.727 867 6	8.132 222 2	13.304 025 4
	8	0.530 181 1	3.727 852 8	8.131 235 3	13.276 893 2
	9	0.530 181 0	3.727 850 0	8.131 011 6	13.268 940 6
	E	0.530 181 0	3.727 849 0	8.130 913 0	13.264 235 6
5	1	3.407 541 3			
	2	2.596 547 3	6.097 722 2		
	3	2.012 651 7	4.496 307 0	10.598 562 8	
	4	1.648 327 2	3.867 547 2	7.993 304 6	16.060 742 5
	5	1.485 771 3	3.592 467 6	6.842 312 6	12.632 164 5
	6	1.434 140 0	3.484 824 6	6.329 078 6	11.044 309 1
	7	1.422 295 8	3.452 733 7	6.136 127 5	10.303 162 5
	8	1.420 247 3	3.445 771 7	6.081 242 5	10.010 082 2
	9	1.419 964 8	3.444 629 3	6.069 756 7	9.922 025 2
	E	1.419 928 6	3.444 459 8	6.067 646 9	9.898 785 4
50	1	295.583 163 3			
	2	230.814 661 0	304.015 701 5		
	3	168.208 745 7	261.850 364 8	307.398 947 1	
	4	118.676 248 4	212.742 642 2	277.539 185 4	309.343 554 4
	5	82.460 036 0	168.560 400 0	238.539 171 1	287.295 054 2
	6	57.125 403 4	132.278 018 4	200.590 335 8	255.757 525 1
	7	39.846 679 4	103.795 656 8	167.158 978 1	223.293 312 6
	8	28.213 826 2	81.954 773 3	139.088 760 3	193.215 486 8
	9	20.484 862 1	65.526 644 9	116.282 709 8	166.916 499 2
	E	4.989 954 5	14.929 342 6	24.807 141 3	34.622 233 2

basis $\{\chi_n\}$ of Eq. (6). Instead we use the so-called moment-generating or Lanczos-like basis to illustrate one particular, but rather general, method that permits a systematic improvement of an *arbitrary* single starting trial function $|\phi\rangle$ that is used in a SSVM treatment.

With any such state $|\phi\rangle$ as a seed or initial wave function, we thus now consider the nonorthogonal basis $\{|X_n\rangle\}$ constructed by repeated action upon it by the full Hamiltonian operator H of the problem under consideration:

$$|X_n\rangle \equiv H^n |\phi\rangle, \quad n=0,1,2,\dots \quad (18)$$

If we define the k th moment of the Hamiltonian as

$$\mu_k \equiv \langle \phi | H^k | \phi \rangle, \quad k=0,1,2,\dots \quad (19)$$

the N th-order MSVM estimates for the lowest N eigenvalues E of H , using the basis $\{|X_n\rangle, n=0,1,\dots,N-1\}$ are obtained from Eq. (3) as

$$\det(\mu_{i+j-1} - E\mu_{i+j-2}) = 0, \quad i,j=1,2,\dots,N. \quad (20)$$

It is trivial to show that Eq. (20) can be equivalently written as

$$\Delta_\phi(E,N) = 0, \quad (21)$$

where $\Delta_\phi(E,N)$ is defined to be the order $(N+1) \times (N+1)$ determinant:

$$\Delta_\phi(E,N) \equiv \begin{vmatrix} \mu_0 & \mu_1 & \cdots & \mu_N \\ \mu_1 & \mu_2 & \cdots & \mu_{N+1} \\ \vdots & \vdots & \ddots & \vdots \\ \mu_{N-1} & \mu_N & \cdots & \mu_{2N-1} \\ 1 & E & \cdots & E^N \end{vmatrix}. \quad (22)$$

As an aside we note that the MSVM employing this moment-generating basis of Eq. (18) has obvious points of

TABLE III. Comparison of exact (E) values with SSVM (S) and ninth-order MSVM estimates (M) for the energies of the lowest four states of the double-well quartic-anharmonic-oscillator potential of Eq. (4) for various values of Z^2 . The variational methods use, respectively, the lowest ($n=0$) only and the lowest nine ($0 \leq n \leq 8$) states of the moment-generating basis of Eq. (18), and with a seed function $\phi(x) = \chi_0(x)$ or $\chi_1(x)$ from Eq. (6), for even and odd states, respectively. The corresponding values of the nonlinear parameter α^2 in the seed function are shown in parentheses, and are chosen to minimize approximately each individual level shown.

Z^2	Method	E_0	E_1	E_2	E_3
0	S	0.540 844 9 (1.44)			
	M	0.530 181 0 (3.00)	1.899 836 5 (3.00)	3.727 849 2 (3.00)	5.822 373 2 (3.25)
	E	0.530 181 0	1.899 836 5	3.727 849 0	5.822 372 8
0.5	S	0.481 761 2 (1.33)			
	M	0.466 258 8 (3.00)	1.698 139 7 (3.00)	3.442 048 6 (3.00)	5.458 186 9 (3.25)
	E	0.466 258 8	1.698 139 7	3.442 048 3	5.458 185 9
1	S	0.477 018 5 (1.21)			
	M	0.453 826 5 (3.00)	1.542 268 1 (3.00)	3.206 951 1 (3.00)	5.144 324 6 (3.25)
	E	0.453 826 5	1.542 268 1	3.206 950 6	5.144 323 1
2	S	0.625 000 0 (1.00)			
	M	0.568 893 0 (3.00)	1.356 514 0 (3.00)	2.891 217 3 (3.00)	4.666 437 6 (3.00)
	E	0.568 892 9	1.356 513 9	2.891 214 8	4.666 434 1
4	S	1.510 338 0 (0.67)			
	M	1.144 828 4 (2.75)	1.376 040 5 (2.75)	2.970 746 9 (2.75)	4.306 513 6 (2.75)
	E	1.144 824 8	1.376 038 7	2.970 718 6	4.306 471 7
5	S	2.228 648 0 (0.56)			
	M	1.419 964 8 (2.75)	1.499 672 3 (2.75)	3.444 629 3 (2.75)	4.415 763 8 (2.75)
	E	1.419 928 6	1.499 662 3	3.444 459 8	4.415 608 1
7	S	4.189 183 7 (0.42)			
	M	1.789 922 9 (2.50)	1.793 919 5 (2.50)	4.856 553 3 (2.50)	5.070 730 0 (2.50)
	E	1.789 447 4	1.793 773 9	4.853 147 4	5.069 000 3
15	S	18.800 000 0 (0.20)			
	M	2.856 571 3 (1.75)	2.822 220 1 (2.00)	8.947 763 2 (1.75)	8.750 227 5 (2.00)
	E	2.704 306 4	2.704 306 4	7.967 640 0	7.967 640 1
30	S	75.025 000 0 (0.10)			
	M	7.945 094 6 (1.00)	6.282 836 5 (1.00)	26.726 708 8 (1.00)	24.007 354 5 (1.25)
	E	3.856 151 8	3.856 151 8	11.499 871 4	11.499 871 4
50	S	208.348 333 3 (0.06)			
	M	20.484 862 1 (0.70)	17.013 680 (0.60)	65.526 644 9 (0.70)	59.018 523 7 (0.70)
	E	4.989 954 5	4.989 954 5	14.929 342 6	14.929 342 6

similarity both with the method of moments²⁷ and with the so-called Padé-Rayleigh-Ritz principles.²⁸ We comment further on the interconnections between these methods in Sec. IV.

In order to compare with the results of Sec. II, we again use the double-well Hamiltonian of Eq. (4), $H \rightarrow H_2$, as our test case. Furthermore, to make the comparison as close as possible we first study the case where the seed wave function $|\phi\rangle$ is itself chosen to be one of the harmonic-oscillator wave functions $\{\chi_n(x)\}$ of Eq. (6). Since H_2 is symmetric under $x \leftrightarrow -x$ and the states of Eq. (6) are parity eigenstates, this choice again ensures that the even- and odd-state spectra separate completely. Thus we first calculate the even and odd spectra separately by making the choices $\langle x|\phi\rangle \rightarrow \chi_0(x)$ and $\chi_1(x)$, respectively. Results of this procedure for the four lowest even states, for example, are shown in Table II for various values of the parameter Z^2 of the Hamiltonian H_2 . For each value of Z^2 , the results are given at various N th-order MSVM estimates, namely, for values of N between 1 (i.e., the SSVM) and 9. For every energy eigenvalue shown the corresponding N th-order MSVM estimates have been calculated for all values of N using that value of the variational parameter α^2 which minimizes that particular energy level at the highest order displayed, namely, $N=9$. One observes that for both the $Z^2=0$ and $Z^2=5$ cases, the convergence is quite rapid, even though in the latter case the starting, $N=1$ (SSVM), estimate to the ground-state energy has a very large error. As expected, the results in the case of the deep double-well potential with $Z^2=50$ are much poorer, although even here the $N=9$ MSVM results are an enormous improvement over the extremely inaccurate SSVM results for this case.

In Table III we compare the exact results with the ninth-order ($N=9$) MSVM results for the lowest four energy levels of the Hamiltonian H_2 of Eq. (4), and with the first-order ($N=1$) SSVM results for the ground-state energy level, for a wide range of values of Z^2 . In each variational calculation the result is shown for the (approximate) value of α^2 which minimizes that particular energy level at the given order of implementation. The associated approximate value of α^2 is itself shown in parentheses. Just as in the case of the previous results in Sec. II which employed the orthogonal basis, we again observe a large difference between the optimal SSVM and MSVM values for the nonlinear parameter α^2 , especially for large values of Z^2 .

The sensitivity of the MSVM results using the moment-generating basis of Eq. (18) to the harmonic-oscillator parameter α^2 in the simple starting function $\langle x|\phi\rangle = \chi_0(x)$ is explored further in Fig. 2. The estimates for the ground-state energy from various orders N of implementation of the method between 1 and 9 are shown for the double-well potential with $Z^2=5$. One observes that just as in the previous case in Sec. II employing the orthogonal basis of Eq. (6), at large orders N there is a very broad region of the variational parameter space that provides a good estimate of the energy. We also observe again that the optimal SSVM ($N=1$) estimate for α^2 is a

FIG. 2. Energy (E_0), as a function of the nonlinear variational parameter α^2 , of the ground state of the double-well quartic-anharmonic oscillator with $Z^2=5$, as calculated via the MSVM using the nonorthogonal moment-generating basis with the single-Gaussian seed function $\chi_0(x)$ of Eq. (6), at various orders N of implementation: $N=1$ (solid line), 2 (dashed line), 3 (dotted line), 6 (dashed-dotted line), and 9 (dashed-double dotted line). Note that the flat region of the $N=9$ curve is indistinguishable from the exact result at this resolution.

very poor choice for higher orders. Indeed, one would have to go to extremely large values of N before the optimal SSVM value was contained in the general “plateau of accuracy” observed at each higher value of $N \gtrsim 5$.

As we have seen, the MSVM can provide a rapid improvement with increasing order of implementation N , of the energy spectrum, even when the starting trial function is far from realistic. However, as we have already remarked, the MSVM can in principle easily take advantage of an improved starting wave function even when it is not a member of a known complete orthogonal set. We shall now use this freedom to choose an intuitively much more accurate starting wave function $|\phi\rangle$ as the seed for the moment-generating basis of Eq. (18). For the double-well Hamiltonian H_2 of Eq. (4), obvious improvements are the even and odd linear combinations $|\phi_{\pm}\rangle = |\phi_{\pm}(\alpha^2, b)\rangle$ of two translationally shifted Gaussians, where

$$\begin{aligned} \langle x|\phi_{\pm}(\alpha^2, b)\rangle &\equiv \exp\left[-\frac{1}{2}\alpha^2(x-b)^2\right] \\ &\pm \exp\left[-\frac{1}{2}\alpha^2(x+b)^2\right], \end{aligned} \quad (23)$$

and which are appropriate for separate MSVM descriptions of the even and odd eigenstates, respectively.

Typical results for the lowest two odd levels, employing the state $|\phi_{-}(\alpha^2, b)\rangle$ as the seed function for the moment-generating basis, are shown in Table IV. For each value of Z^2 , the parameters α^2 and b have been optimized at the SSVM ($N=1$) level and then used for all

TABLE IV. Values for the MSVM estimates of the energies of the lowest two odd levels of the double-well quartic-anharmonic-oscillator potential of Eq. (4) for various values of Z^2 , and at various orders N of implementation, using the nonorthogonal moment-generating basis of Eq. (18) with the double-Gaussian seed function $|\phi_-(\alpha^2, b)\rangle$ of Eq. (22). The values of the nonlinear parameters α^2 and b shown are in each case chosen to minimize the estimate for E_1 at the $N=1$ (SSVM) level. The results marked E in the N (order) column are exact.

Z^2	α^2	b	N	E_1	E_3
0	3.0542	0.7929	1	1.900 778 1	
			2	1.899 847 2	16.285 165 4
			3	1.899 838 9	16.026 220 7
			4	1.899 838 1	15.886 230 3
			5	1.899 837 4	10.904 251 4
			6	1.899 836 9	7.445 228 5
			7	1.899 836 7	6.603 960 4
			8	1.899 836 6	6.319 136 7
			9	1.899 836 6	6.176 372 3
			10	1.899 836 5	6.083 887 7
			E	1.899 836 5	5.822 372 8
0.5	3.0009	0.8357	1	1.699 414 8	
			2	1.698 155 9	15.712 300 4
			10	1.698 139 7	5.566 072 5
			E	1.698 139 7	5.458 185 9
2	2.869	0.988	1	1.359 824 4	
			2	1.356 596 0	14.421 297 3
			10	1.356 514 5	5.269 832 9
			E	1.356 513 9	4.666 434 1
4	2.856	1.263	1	1.387 182 2	
			2	1.376 663 1	13.504 609 6
			10	1.376 046 6	6.828 444 5
			E	1.376 038 7	4.306 471 7
7	3.510	1.753	1	1.814 068 8	
			2	1.796 123 2	13.671 990 1
			10	1.793 787 8	8.028 183 5
			E	1.793 773 9	5.069 000 3
15	5.371	2.687	1	2.713 139 6	
			2	2.704 706 4	19.343 880 4
			10	2.704 306 4	11.095 294 6
			E	2.704 306 4	7.967 640 1
50	9.9459	4.9848	1	4.992 493 3	
			2	4.989 968 7	35.148 900 2
			5	4.989 954 6	30.047 525 4
			E	4.989 954 5	14.929 342 6

higher MSVM orders N shown. We note both that the $N=1$ results for E_1 are accurate to about 1% or better, and that the convergence to the exact results is rapid for each value of Z^2 as the basis size N is increased. On the other hand, the corresponding results for the energy E_3 of the second odd level are both very noticeably less accurate and slower to converge. In this latter regard, a part of the reason for this slowed convergence is a marked tendency for the results to “pin” to some *higher* level. For example, the $Z^2=0$ data demonstrate that the lowest-order $2 \leq N \leq 4$ MSVM results for E_3 are all pinning very close to the exact result for the fourth odd level E_7 (≈ 16.05). At $N=5$ the MSVM estimate for E_3 then suddenly drops to a value near the exact E_5 (≈ 10.62). Finally, for higher values of N , the corresponding esti-

mate again “depins” and thereafter converges smoothly to the exact value of E_3 .

Table IV also clearly demonstrates the expected result that for higher values of Z^2 , namely, for deep wells, the optimal value of the parameter b becomes closely equal to the value $2^{-1/2}Z$ which marks the positions of the potential minima. In Figs. 3 and 4 we examine more closely the sensitivity of our results for the ground-state energy E_0 to the choices of the two nonlinear variational parameters α^2 and b , for the respective cases of the SSVM ($N=1$) and ninth-order MSVM ($N=9$) calculations. Figure 3 clearly illustrates a noticeably more marked sensitivity to the parameter b than to the parameter α^2 . The $N=9$ results in Fig. 4 demonstrate the expected broader plateau of accuracy in the (α^2, b) space than for the corre-

FIG. 3. Accuracy (as defined in Fig. 1), as a function of the nonlinear variational parameters α^2 and b , of the ground-state energy E_0 for the double-well quartic anharmonic oscillator with $Z^2=5$, as calculated with the SSVM and the double-Gaussian trial wave function $\langle x|\phi_+(\alpha^2, b)\rangle$ of Eq. (22). The data are represented as a contour plot, with each dashed contour showing a value of the accuracy equal to zero (outermost contour) or some positive integral value, and with each intervening solid contour representing an increase in accuracy of 0.25. The point marked represents the highest accuracy attainable at this level.

sponding $N=1$ results. Although the steep ridge in the accuracy surface at around $b \approx 1.4$ still persists at $N=9$, the surface nevertheless also contains a great deal of additional detail which is not easily intuited.

Finally, in Table V we examine three particular points in the (α^2, b) space in more detail in order to compare closely the accuracy attainable in various orders from various starting approximations. These three points refer respectively to the choice for the seed function $|\phi\rangle$ in Eq. (18) as the single Gaussian $|\chi_0\rangle$, with the parameter α^2 chosen to minimize approximately the corresponding MSVM estimate for E_0 at order $N=9$, and the even combination $|\phi_+(\alpha^2, b)\rangle$ with the two choices for the parameters (α^2, b) which minimize the estimate for E_0 at either first order (SSVM) or ninth order (MSVM). In the first place we see again the large difference between the optimal choices, which depend strongly on the order N of implementation. We also observe that optimization of a particular level (here E_0) at a given order, does not guarantee optimal or even good results for the other levels. Thus the values of (α^2, b) which minimize E_0 at the $N=9$ order are producing a value for E_6 which appears to be converging, but which instead is “pinning” to a value close to the eigenvalue $E_8 \approx 14.4432$. In fact, the most accurate of the three estimates for E_6 displayed in Table V comes from that based on the single Gaussian seed function. Furthermore, a comparison of the first two sets of results gives a particularly striking illustration of the importance of optimizing the nonlinear variational

FIG. 4. As in Fig. 3, but calculated with the MSVM using the moment-generating nonorthogonal basis built on the corresponding SSVM trial function of Fig. 3 as the seed function, and at order of implementation, $N=9$.

parameters. Thus we see clearly that the more restricted single-Gaussian choice of seed function gives better values for each of the lowest four even levels displayed at order $N=10$ than the corresponding calculation based on a double Gaussian seed function, if the former is optimized for E_0 at a higher order N of implementation, whereas the latter is optimized only at the SSVM level.

IV. DISCUSSION

Both the single- and double-well quartic anharmonic oscillators have been much studied in the past by authors whose main motivation has been to consider them either as the $(0+1)$ -dimensional model analogs of the comparable quantum field theories in higher numbers of dimensions, or as models on which to test various forms of many-body perturbation theory. For example, since many of the earliest results in such quantum field theories as quantum electrodynamics had been obtained from perturbation theory, the precise nature of the perturbation series for such simple Hamiltonians as the single-well anharmonic potential of Eq. (9) was studied by Bender and Wu,²⁹ Simon,³⁰ and other authors. These authors investigated the asymptotic nature of the corresponding perturbation series when the unperturbed Hamiltonian is simply taken as the corresponding $\lambda=0$ limit of the full Hamiltonian, namely, that of Eq. (7) with $\alpha^2=1$. The resulting Rayleigh-Schrödinger series was shown to be divergent for all values of the coupling constant λ by Bender and Wu,²⁹ who used Wentzel-Kramers-Brillouin (WKB) methods to demonstrate explicitly the exponentially unbounded asymptotic behavior of the high-order terms in the series.

In view of the asymptotic nature of the above perturbation series, various resummation techniques have been applied with varying degrees of numerical success.^{30–33} Typical of these are the method of Padé approximants,³⁰

TABLE V. Values for the MSVM estimates of the energies of the lowest four even levels of the double-well quartic-anharmonic-oscillator potential of Eq. (4) with $Z^2=5$, and at various orders N of implementation. The basis used is the nonorthogonal moment-generating basis of Eq. (18) with the double-Gaussian seed function $|\phi_+(\alpha^2, b)\rangle$ of Eq. (22). The three sets of (α^2, b) values used respectively approximately minimize the estimates for E_0 at order $N=9$ with $b=0$, at order $N=1$, and at order $N=9$. The row of results marked E are exact.

b	α^2	N	E_0	E_2	E_4	E_6
0.0	2.75	1	3.407 541 3			
		2	2.596 547 3	6.097 722 2		
		3	2.012 651 7	4.496 307 0	10.598 562 8	
		4	1.648 327 2	3.867 547 2	7.993 304 6	16.060 742 5
		5	1.485 771 3	3.592 467 6	6.842 312 6	12.632 164 5
		6	1.434 140 0	3.484 824 6	6.329 078 6	11.044 309 1
		7	1.422 295 8	3.452 733 7	6.136 127 5	10.303 162 5
		8	1.420 247 3	3.445 771 7	6.081 242 5	10.010 082 2
		9	1.419 964 8	3.444 629 3	6.069 756 7	9.922 025 2
		10	1.419 932 7	3.444 481 1	6.067 951 6	9.903 010 7
1.4	2.7	1	1.471 862 7			
		2	1.435 669 0	11.475 437 9		
		3	1.428 885 5	9.097 041 6	26.606 879 5	
		4	1.425 947 7	7.710 536 7	18.619 513 3	48.624 194 7
		5	1.424 142 8	6.634 535 8	14.977 675 3	36.115 886 3
		6	1.422 959 6	5.852 775 8	13.139 156 8	29.971 736 0
		7	1.422 176 2	5.319 543 0	12.087 072 3	26.131 625 5
		8	1.421 640 8	4.950 108 5	11.387 298 2	23.359 028 7
		9	1.421 258 6	4.681 522 5	10.859 218 7	21.190 230 7
		10	1.420 976 4	4.477 991 5	10.426 226 6	19.444 716 9
0.5	3.5	1	2.879 512 7			
		2	2.048 473 5	4.568 086 2		
		3	1.712 252 8	3.988 028 8	14.638 561 6	
		4	1.524 783 9	3.682 162 5	8.205 167 7	21.372 987 9
		5	1.438 822 0	3.498 537 7	6.466 837 0	17.671 429 4
		6	1.422 467 2	3.453 273 9	6.142 174 8	15.880 657 9
		7	1.420 221 6	3.445 648 8	6.079 879 8	14.962 144 9
		8	1.419 956 9	3.444 590 1	6.069 254 0	14.578 827 5
		9	1.419 930 9	3.444 471 5	6.067 819 9	14.466 310 9
		10	1.419 928 8	3.444 461 0	6.067 671 0	14.444 205 2
		E	1.419 928 6	3.444 459 8	6.067 646 9	9.898 785 4

the method of continued fractions,³¹ and the Borel summability method.^{32,33} Such methods often give very good results for not too high values of the coupling constant ($\lambda \lesssim 1$), but are still problematic for higher values.

Further renormalizations of the perturbation series in order to increase the overall numerical accuracy of the resulting approximations for the energy levels, and the application of such techniques to both single- and double-well anharmonic oscillators, have been discussed by many authors.^{24,34–39} The basic aim of all such methods has been to repartition the full Hamiltonian into an unperturbed and a perturbed part. Of particular interest in the present context is the technique of introducing auxiliary free parameters^{24,36} into the unperturbed Hamiltonian in order to improve the accuracy or convergence properties. For the anharmonic oscillators, the unperturbed Hamiltonian has typically been chosen in the form of Eq. (7). Within this perturbative framework, Caswell³⁶ has discussed a criterion for choosing an optimal value of the parameter α^2 which is identical to our

Eq. (11), and hence independent of the order N at which the resulting perturbation series is terminated. Conversely, Killingbeck,²⁴ arguing by analogy with the fact that the exact results are independent of the auxiliary parameter α^2 , discusses the use of the simple yet very accurate order-dependent criterion that the variation with respect to α^2 of the N th-order approximation $E_0^{(N)}$ to the ground-state energy, say, should vanish, $dE_0^{(N)}/d\alpha^2=0$.

In precisely the same spirit to the above perturbation-theoretic investigations, the coupled-cluster method (CCM)^{40,41} has also been applied recently to the problem of anharmonic oscillators.²⁶ The CCM is nowadays regarded as one of the most powerful, most universal, and most accurate of all formulations of quantum many-body theory.⁴¹ It has successfully been applied to a wide range of physical systems including, for example, atomic and molecular systems in quantum chemistry, finite nuclei, nuclear matter, the one-component Coulomb plasma (or “electron gas”), and model systems in quantum field theory. Although the CCM has its ultimate origins in

Goldstone perturbation theory, it may nowadays safely be viewed as a fundamental formalism in its own right. Nevertheless, at any particular level of truncation in one of its hierarchies of approximations which are necessary for practical calculations, the resulting closed set of equations for the many-body cluster amplitudes considered at that level of approximation, may formally be iterated and hence regarded as a particular (and very complex) partial, but infinite, resummation of the entire perturbation series.

The CCM calculations in the field of quantum chemistry are perhaps of particular interest for present purposes. Thus the short-distance singularity in the Coulomb interaction between electrons has the effect of producing cusps in the wave functions, and hence special interest needs to be given to the choice of single-particle orbitals for the basis in which the CCM equations are expanded. The standard choice for these basis states is the complete set of orbitals from the lowest of which the Slater-determinantal reference state (for closed-shell systems) or multireference states (for open-shell systems), are constructed. Very extensive work has been performed in quantum chemistry in connection with this question of generating adequate basis sets. The usual procedure has been to optimize different sizes of basis sets for individual atoms by the Hartree-Fock (HF) method. Such self-consistent (at the one-body level) HF orbitals are then commonly used in molecular calculations employing either the CCM or various implementations of the MSVM considered here, for example.

However, the singular cusps in the wave functions are not easily able to be represented by an expansion in a small number of single-particle orbitals, however optimized these may be. A consequence is that instabilities may arise in numerical solutions of the CCM equations. Even in the much simpler calculations using standard many-body perturbation theory (MBPT), it is typically found for molecules that the error in the correlation energy which fundamentally arises from the size and quality of the basis set is at least one order of magnitude greater than the energy contribution from the difficult to calculate fourth- and higher-order terms. Indeed, it has been pointed out by Wilson and Silver⁴² that it might be more reasonable to improve the basis set and retain terms up to only the third-order level of perturbation theory, rather than pursue the small additional residue coming from the fourth-order terms and beyond.

One way of circumventing all of the above problems, within both the MBPT and the CCM calculations, is to use the so-called geminal expansions in which the single-particle orbitals are replaced by explicitly correlated functions.⁴³ A typical geminal thus comprises the product of a pair of single-electron orbitals together with a correlation factor that depends explicitly on the distance between the two electrons. If the single-particle (HF) orbitals are expanded in Gaussian basis functions and the correlation factors are also taken to be Gaussian functions of the interparticle distance, both the resulting many-electron integrals in the case of MBPT, and the CCM equations, can be handled relatively easily. Such Gaussian geminal bases were introduced into quantum

chemistry by Boys⁴⁴ and Singer,⁴⁵ and have been extensively used thereafter for calculations using the MSVM,⁴⁶ MBPT,^{47–49} and the CCM.^{50,51} In practical applications one usually has the by now familiar situation of working with both linear coefficients, which are readily optimized variationally, and exponential (nonlinear) variational parameters. Even in the context of MBPT, the second-order correlation energy, for example, can rather accurately be calculated by minimizing an appropriate second-order energy functional,⁴⁹ within the basis of Gaussian-type geminals.

This change to a geminal basis in the CCM, for example, often has the effect of reducing by many orders of magnitude the number of terms needed for a given level of accuracy in representing the cluster amplitudes. Consequently, the amount of computer time needed for a given accuracy is also reduced, although not by the same factor since the geminal basis is itself more complicated. However, it is once again typically found both in the MBPT calculations^{47–49} and in the CCM calculations^{50,51} that a careful optimization of the nonlinear parameters is vital to obtain accurate results or, equivalently, to obtain satisfactory pair functions with relatively few terms. Indeed, the search for optimal values of the nonlinear parameters often turns out to be the computationally most time-consuming part of the calculation.

Returning to a more general discussion of the CCM, the nature of the convergence of the resulting set of approximations for the ground-state energy, as a function of the truncation index that labels the level of approximation, is also of great interest. The quartic anharmonic oscillators have again formed a key model system in this regard.²⁶ The starting point of the CCM is a model or uncorrelated wave function against which to measure the many-body correlations. It can be chosen rather freely. For the model anharmonic oscillator problems it is most obviously taken to be the vacuum state associated with the corresponding harmonic-oscillator problem. In the CCM context it is also rather natural to consider a Bogoliubov transformation of the associated creation and destruction operators (or ladder operators), as the most general linear canonical transformation between them. Although the exact, fully correlated theory is again independent of the choice of model wave function, the numerical accuracy at a given level of approximation may be improved by an appropriate choice of the coefficients of this Bogoliubov transformation. One such choice is the so-called Hartree approximation, which for the single-well potential of Eq. (9), for example, again leads precisely to the model wave function $|\chi_0\rangle$ of Eq. (6) as the renormalized vacuum state, and with the choice of parameter α^2 given by the criterion of Eq. (8), or explicitly by Eq. (11). For the double-well potential of Eq. (4), it also leads rather naturally to the shifted Gaussian state $\chi_0(x-b)$ as the model wave function, with both parameter α^2 and b determined analogously. The accuracy of the resulting CCM calculations has been discussed in detail by two of the present authors.²⁶

In light of the above discussion, the present work may be viewed as an attempt to apply an analogous critique for what is probably the most accurate and most widely

applicable of the remaining microscopic formulations of quantum many-body theory, namely, the (Jastrow) variational method and its systematic improvement via the method of correlated basis functions.^{12,14,52} One knows that in general the success of a variational calculation depends quite crucially on the choice of the basis functions. Furthermore, just as in the perturbative calculations involving auxiliary parameters in the unperturbed Hamiltonian, so it has been found that the accuracy of the variational calculations can depend sensitively on the choice of any nonlinear free parameters that characterize the basis functions. The case of an orthogonal basis bears a close resemblance to both the perturbative methods and the CCM, as discussed above. As we have described in the present paper, the optimal MSVM choice of parameter α^2 can be very different from the optimal SSVM choice. We have discussed a rather simple order-dependent criterion which works very well in practice for the ground-state and other energy levels. In many ways this criterion plays a similar role within the variational methodology to that of Killingbeck²⁴ mentioned previously within the framework of perturbation theory.

A further discussion of the perturbation criterion of Killingbeck has been given very recently,⁵³ and is of particular interest in the present context. These authors address the question of whether the N th-order perturbative estimate for the i th bound-state eigenfunction of the single-well quartic anharmonic oscillator is a good approximation to the exact one, when the parameters α^2 and N are fixed by the Killingbeck criterion for the corresponding i th energy eigenvalue. In order to attempt to answer this question, they adopt as a new criterion to choose α^2 that the norm of the N th-order term in the perturbation expansion for the given energy eigenfunction should be as small as possible. They show that the energy criterion and the norm criterion are by no means equivalent. In particular, for the ground and low-lying states the minimum contribution to the norm of the wave functions occurs for lower values of N than those which minimize the perturbative contribution to the energy eigenvalue. These authors also observe that if the perturbative approximation to a given energy eigenfunction is good, the corresponding energy eigenvalue when calculated as the expectation value of the Hamiltonian in this approximate state, should also be a good (variational) estimate.

Thus they also use successive perturbative approximations to the energy eigenfunctions as trial states for a variational calculation, and use the minimization of the corresponding estimate for each eigenenergy as a further criterion to choose the constants α^2 and N . Clearly, the variational principle can only rigorously be used to justify this latter criterion for the ground state, since the perturbatively derived trial wave function for a given excited state is not exactly orthogonal to the subspace containing all of the exact lower eigenfunctions. It is then perhaps not too surprising that while this variational criterion is essentially equivalent for the ground state to that based upon the variation of the norm of the perturbative correction to the wave function, this is not true for the higher states. Furthermore, since it is well known that

use of an N th-order perturbative approximation to the (ground-state) wave function in a variational estimate of the energy gives essentially the corresponding perturbative result for the energy at $(2N+1)$ th order,⁵⁴ it is also clear, firstly, why both the variational criterion for the energy and the norm criterion for the wave function differ from Killingbeck's energy criterion when compared by order and, secondly, why the optimal accuracy in the energy is the same, by both energy criteria, at least for the ground state.

Within the MSVM framework considered in the present paper, one may also wonder to what extent the Rayleigh-Ritz variational principle, which gives the best energy estimate compatible with the basis, also gives a wave function with the same property. In general, although we know by the interlace theorem that by increasing the basis size N the energy eigenvalues tend monotonically to the exact values from above, it is quite possible that the wave functions themselves may become worse. One such measure of the accuracy of the wave function is, for example, the variance of the energy in the trial wave function $|\phi\rangle$, namely, $\langle\phi|[H-E(\phi)]^2|\phi\rangle$, where $E(\phi)=\langle\phi|H|\phi\rangle/\langle\phi|\phi\rangle$. It is often found that the variance can increase with N , particularly when the trial basis is ill suited to the problem at hand, as in the case of the harmonic-oscillator basis centered at the origin for the deep double-well anharmonic oscillator of Eq. (4). A particularly interesting discussion of this point has been given by Schiffrer and Stanzial.⁵⁵

These authors consider a somewhat different criterion to choose, for example, the nonlinear variational parameter α^2 of the harmonic-oscillator basis. It is not based on minimizing the Rayleigh-Ritz estimate for the energy. Instead, they first introduce projection operators P and $Q \equiv 1 - P$, which, respectively, project into and out of the M -dimensional model space spanned by the (generally nonorthogonal) set of linearly independent trial basis functions $\{|\chi_n\rangle; n=1, 2, \dots, M\}$,

$$P \equiv \sum_{m=1}^M \sum_{n=1}^M |\chi_m\rangle (\mathcal{N}^{-1})_{mn} \langle\chi_n|, \quad (24)$$

where $\mathcal{N}_{mn} \equiv \langle\chi_m|\chi_n\rangle$ is the $(M \times M)$ -dimensional normalization matrix. By projecting the exact Schrödinger equation

$$(H - E)|\psi\rangle = 0 \quad (25)$$

into and out of the model space, and hence eliminating the component $Q|\psi\rangle$ out of the model space, it is simple to show that Eq. (25) may be exactly rewritten wholly within the model space as

$$P[H - E + W(E)]P|\psi\rangle = 0, \quad (26)$$

where

$$W(E) \equiv HQ(E - QHQ)^{-1}QH. \quad (27)$$

If we then approximate $W(E)$ by zero, we are left with the problem of diagonalizing the truncated $(M \times M)$ -dimensional matrix PHP , which as we have seen is exactly equivalent to our MSVM.

Schiffrrer and Stanzial⁵⁵ thus argue that it is natural to intuit that the MSVM procedure will give the best results when the norm of the matrix $PW(E)P$ is minimized with respect to α^2 , so that the exact and approximate problems become closest in this sense. An exact implementation of this criterion is difficult due to the explicit dependence on the unknown energy eigenvalue E of the Q -space resolvent, $(E - QHQ)^{-1}$, of the Hamiltonian. These authors therefore consider a simplified version, and show how their modified criterion can also give very good numerical accuracy in the case of the deep double-well potential of Eq. (4), using our orthogonal centered harmonic-oscillator basis of Eq. (6). However, even their simplified criterion is considerably more complicated than our own, which, in turn we have seen is close to being the absolute optimum for the energies of this problem. Nevertheless, a further comparison of the precision of the two methods for the corresponding wave functions would be of interest.

Finally, we remark that the use of the nonorthogonal moment-generating basis that we have also discussed within the MSVM as a means of improving the basis to tailor it more closely to the underlying physics of the problem at hand, may also usefully be viewed as an extension of the usual single-state Rayleigh-Ritz method (SSVM) in the following sense discussed by Bessis and his co-workers.²⁸ Given a single reference state $|\phi\rangle$, one knows that a full knowledge of the resolvent $R(E; \phi)$ of the Hamiltonian H with respect to the state $|\phi\rangle$,

$$R(E; \phi) \equiv \langle \phi | (E - H)^{-1} | \phi \rangle, \quad (28)$$

often completely suffices for most purposes. For example, the poles of the resolvent in the E space provide the location of the bound-state energy eigenvalues. Using the moments defined in Eq. (19), we may formally expand the resolvent in the (asymptotic) series,

$$R(E; \phi) = \sum_{k=0}^{\infty} \mu_k E^{-k}. \quad (29)$$

The usual Rayleigh-Ritz principle provides, as the SSVM, an estimate of the exact ground-state-energy eigenvalue E_0 from a knowledge of just the first two terms μ_0 and μ_1 of this expansion. The so-called Padé-Rayleigh-Ritz principle extends this procedure by providing a method to give the best possible bounds for the energies $E_0, E_1, \dots, E_N$ of the lowest N states, given a knowledge of the first $2N$ terms, $\mu_0, \mu_1, \dots, \mu_{2N-1}$ in the expansion of the resolvent of Eq. (29).

Bessis and his colleagues demonstrate²⁸ that this is explicitly achieved by setting to zero the denominator of the $[N/N]$ Padé approximant for the resolvent. They further show that this denominator is precisely the determinant $\Delta_\phi(E, N)$ of Eq. (22), the roots of which, as we have seen in Sec. III, are precisely equivalent to the energy estimates given by our own MSVM technique based upon the moment-generating basis of Eq. (18). It is therefore clear that the MSVM, and the necessary optimiza-

tion of the basis that we have discussed here in detail, may also make useful contributions to the method of moments,²⁷ which is yet another technique that has been widely applied to many-body systems.

From this latter viewpoint it is also interesting to speculate whether the Padé technique might usefully be applied in a similar way to expectation values of other functions of the Hamiltonian. An obvious candidate in this regard is the "propagator" function

$$G(t; \phi) \equiv \langle \phi | e^{-Ht} | \phi \rangle, \quad (30)$$

since, for example, the ground-state energy E_0 is readily extracted from it as

$$E_0 = - \lim_{t \rightarrow \infty} \frac{d}{dt} [\ln G(t; \phi)]. \quad (31)$$

The function $\ln G(t; \phi)$ may again readily be expanded in powers of t as

$$\ln G(t; \phi) = \sum_{k=1}^{\infty} \frac{(-t)^k}{k!} M_k, \quad (32)$$

where the parameters $\{M_k\}$ are the usual cumulants associated with the moments $\{\mu_k\}$. Since we know from Eq. (31) that the slope of $\ln G(t; \phi)$ at large t is a constant (namely, $-E_0$), we may now similarly seek $[N/N]$ Padé approximants for the quantity $t^{-1} \ln G(t; \phi)$. The $[0/0]$ approximant just gives the usual variational estimate again. Since the higher Padé approximants now have no obvious variational basis we do not pursue this matter further here, although preliminary calculations indicate that this technique can also profitably be applied to the anharmonic-oscillator problems.

In conclusion, we have shown how the variational methods can, in common with most other important methods of quantum many-body theory, be profitably tested on the model anharmonic-oscillator problems, particularly with regard to the optimization of any nonlinear undetermined parameters within the chosen basis. In so doing, we have uncovered and discussed a number of similarities and links between the MSVM and various of these other techniques. Such links are likely to be useful in applications to many-body systems.

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