Reliability of high-order phase-integral eigenvalues for single and double minimum potentials

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For single and double minimum model potentials, energy eigenvalues are calculated using the Fröman and Fröman phase-integral approximations and compared with exact (numerical) quantum mechanical results. For the double minimum potential, results are obtained both from the correct phase-integral quantization condition including quantum effects near the barrier maximum (the σ term) up to and including the fifth-order approximation, and from the quantization condition with the σ term neglected up to and including the 13th-order approximation. When the σ term is included, the third- and fifth-order eigenvalues are accurate enough for all practical purposes, even close to the barrier maximum, but if the σ term is neglected, the phase-integral quantization condition breaks down near the barrier maximum, and this breakdown becomes more dramatic with increasing order. This property is used to discuss the question of which order of phase-integral approximation will give the optimum result. For a single minimum LJ(12,6) potential, phase-integral eigenvalues are calculated up to and including the 13th-order approximation. In this case, the phase-integral approximations appear able to yield much higher accuracy than can be practically obtained by quantal calculations using existing numerical methods. The reliability of phase-integral eigenvalues at energies near the dissociation limit is discussed, and a generalization of an earlier criterion for the onset of the breakdown of higher-order phase-integral quantization conditions near the asymptote of a potential with an attractive inverse-power $r^{-\nu}$ long range tail (where $\nu > 2$) is given.

I. INTRODUCTION

The efficient determination of accurate eigenvalues for arbitrary single and double minimum potentials is a problem of continuing interest. In principle, such results may always be obtained by direct numerical solution of the one-dimensional Schrödinger equation.[1,2] However, obtaining results of very high accuracy using these "exact" methods is at best laborious, since it requires the use of a very dense integration mesh or a very large basis set. Moreover, for high quantum numbers or energies lying very near a potential asymptote, the accelerating effects of accumulated truncation error make these direct methods increasingly unstable.

An alternative approach to this problem is provided by higher-order phase-integral techniques, which have been attracting increasing attention in recent years.[3–14] This type of approach is computationally much less expensive than exact numerical methods, and high quantum numbers or proximity to a potential asymptote or barrier maximum introduce no additional computational difficulties. On the other hand, although readily able in most circumstances to provide results of extremely high accuracy, the phase-internal method is in principle not exact, so its region of validity should be very carefully investigated. For example, the simple (uncorrected) phase-integral quantization condition in either first- or higher-order breaks down at a potential barrier maximum, while only the first-order quantization condition is stable at energies near the asymptote of a potential with a realistic inverse-power long-range tail. Correction terms which prevent the breakdown in the former case and evidence that the breakdown region is not physically significant in the latter were presented previously.[15] The present work attempts to clarify those results and to delineate when (if ever) high-order phase-integral approximations *should not* be used.

For a double minimum potential, limited tests of the accuracy of phase-integral eigenvalues for various orders of the approximation were reported previously.[7–9] However, only first-, third-, and fifth-order eigenvalues were calculated,[8,9] and their precision was limited by the relatively crude numerical methods then being used. Moreover, the significance of those results was difficult to ascertain because of the limited accuracy of the numerical eigenvalues available for comparison.[16]

In the following, Sec. II provides a brief description of the methods used in the calculations of the quantal and phase-integral results reported here. Section III presents improved quantum mechanical eigenvalues for the same model double minimum potential considered earlier,[7–9,16] compares them with $(2N+1)$th order phase integral eigenvalues for $N=0-6$, and examines the effect of the "σ correction" to the phase integral quantization conditions for $N=0-2$. This section also examines the question of how one knows which value of the order $2N+1$ yields the optimum result for a given case.

The unreliability of higher-order phase-integral quantization conditions for levels lying very near a potential asymptote was first suggested by comparison of quantal eigenvalues with phase-integral results (of order 1, 3,

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and 5) for a particular LJ(12, 6) model potential.[15] It was then shown that this breakdown occurs for *all* potentials with an attractive inverse-power $r^{-\nu}$ long range tail for which $\nu > 2$, and a criterion for predicting the onset of this behavior was devised which suggests that usually no observable bound levels lie in this region.[15] However, the numerical result and the criterion were only obtained up to fifth-order ($2N+1=5$). For this illustrative model problem, Sec. IV extends the numerical results up to 13th order and the breakdown criterion to seventh order. Section V then summarizes our conclusions about the utility of higher-order phase-integral approximations in calculations using realistic single or double minimum potentials.

II. DESCRIPTION OF METHODS USED

For both single and double minimum potentials, the problems considered can be described by the one-dimensional Schrödinger equation in the dimensionless form

$$\frac{d^2\psi}{dz^2} + B_z[\bar{E} - \bar{V}(z)]\psi = 0 , \tag{1}$$

where $B_z = 2\mu\epsilon_s(x_s)^2/\hbar^2$ is a dimensionless potential strength parameter,[17] ϵ_s and x_s are appropriately chosen energy and length scaling parameters, $z = x/x_s$ is the dimensionless distance coordinate, and $\bar{E} = E/\epsilon_s$ and $\bar{V}(z) = V(x)/\epsilon_s$ are the reduced eigenenergy and potential energy function. Note that throughout this paper, a bar over the symbol for a variable indicates that it is dimensionless, with energies and lengths scaled by ϵ_s and x_s, respectively.

For the single minimum potential considered here, $V(x) \to \infty$ as $x \to 0$ and $V(x) \to 0$ as $x \to \infty$, so the allowed eigenvalues are negative and correspond to wave functions satisfying the boundary condition $\psi(z) \to 0$ at both $z \to 0$ and $z \to \infty$. The double minimum potential considered is symmetric about a barrier maximum located at $x = 0$, so the allowed eigenstates all correspond to $\psi(z) \to 0$ as $z \to \pm\infty$ and either $d\psi(z=0)/dz = 0$ or $\psi(z=0) = 0$; the former condition yields the even solutions (labeled +) and the latter the odd solutions (labeled −).

A. Calculation of quantum mechanical eigenvalues

For either single or double minimum potentials, Eq. (1) may be readily solved using standard numerical techniques[1,2]; the results reported below were obtained using a program based on the Numerov integration algorithm of Refs. 2. This method is insensitive to proximity to a potential barrier maximum. However, at very high energies or for potentials with very steep walls, the small integration mesh which must be used if results of high accuracy are to be obtained makes the calculations relatively time consuming and requires the storage of relatively large arrays. For example, achieving the eight-decimal place accuracy of the eigenvalues presented in Sec. III required a potential array size of 20 000. Calculations for levels lying very near a potential asymptote also require the use of very large arrays,[15] not because of a small mesh size requirement, but rather because the slow decay of the long-range tail of the wave function requires the use of a very broad range of integration.

B. Calculation of phase-integral eigenvalues

For a single minimum potential, the phase-integral quantization condition defines the $(2N+1)$th order eigenvalues as the energies E which yield nonnegative integer values of v when substituted into the equation

$$v + \tfrac{1}{2} = \alpha(E)/\pi = (1/\pi)\sum_{n=0}^{N} \alpha^{(2n+1)}(E) , \tag{2}$$

where

$$\alpha^{(2n+1)}(E) = \mathrm{Re}\left\{\frac{1}{2}\oint_{\Gamma_\alpha} dz\, q^{(2n+1)}(z)\right\} = \mathrm{Re}\left\{\frac{1}{2}\oint_{\Gamma_\alpha} dz\, p^{(2n+1)}(z)\right\} . \tag{3}$$

The functions $q^{(2n+1)}(z)$ are known up to very high orders,[3-6,18,19] and the functions $p^{(2n+1)}(z)$ are obtained in a nonunique way upon integration by parts. Making use of the arbitrarily chosen length and energy scaling factors introduced above, x_s and ϵ_s, the usual form of $p^{(2n+1)}(z)$ corresponds to

$$\bar{p}^{(1)}(z) = \sqrt{B_z}\,[\bar{E} - \bar{V}(z)]^{1/2} . \tag{4}$$

For $n = 0$–3 explicit expressions for $\bar{p}^{(2n+1)}(z)$, as functions of $[\bar{E} - \bar{V}(z)]$ and its derivatives with respect to z, are listed in the Appendix. The contour Γ_α appearing in Eq. (3) is a path in the complex plane which encloses and does not cross the cut on the real line running between the two classical turning points z_1 and z_2 associated with a given reduced energy $\bar{E}$, where $\bar{V}(z_1) = \bar{E} = \bar{V}(z_2)$.

For a symmetric double minimum potential, the quantization condition analogous to Eq. (2) is[7]

$$v + \tfrac{1}{2} = \alpha(E)/\pi - \sigma(E)/\pi \pm (1/2\pi)\arctan\{\exp[-K(E)]\} , \tag{5}$$

where

$$K(E) = \sum_{n=0}^{N} K^{(2n+1)} = (i/2)\oint_{\Gamma_K} dz \left\{\sum_{n=0}^{N} q^{(2n+1)}(z)\right\} = (i/2)\oint_{\Gamma_K} dz \left\{\sum_{n=0}^{N} p^{(2n+1)}(z)\right\} \tag{6}$$

and

$$\sigma(E) = \sum_{n=0}^{N} \sigma^{(2n+1)}(E) \tag{7}$$

is the barrier maximum phase correction (see below), while $\alpha(E)$ is a contour integral of the same type as that appearing in Eq. (3). At energies below the barrier maximum, the contour Γ_α associated with $\alpha(E)$ encloses the classically accessible region in one of the wells in exactly the same manner as in the case of the single minimum potential, while Γ_K is an anlogous contour about the classically inaccessible potential barrier region whose direction is chosen so that $K(E)$ will be positive at energies below the barrier maximum. At energies above the potential barrier maximum, the contours Γ_α and Γ_K enclose the transition points in the manner described in Refs. 8 and 9.

The upper sign preceding the last term in Eq. (5) yields the symmetric (denoted +) solutions and the lower sign the antisymmetric ones (denoted −). Note that the definition of the vibrational quantum number v differs in Eqs. (2) and (5). In the former its value indicates the total number of nonboundary wave function nodes, or the total number of levels lying below the one in question. In contrast, in Eq. (5) it indicates the number of nonboundary wave function nodes lying on each side of the barrier maximum, or the number of lower levels of the same (+ or −) symmetry.

A family of recently developed techniques[11–14] allows the contour integrals appearing in Eqs. (3) and (5) to be evaluated readily to virtually any desired accuracy, solely from a knowledge of the potential and its derivatives on the real line. However, while extremely efficient and easy to use for calculations in the lower orders (say, $2N+1$, 3, or 5) this approach becomes increasingly complicated with increasing N. An earlier numerical approach, which is equally reliable, is closely related to the analytic methods for evaluating such integrals[3–9] in that it involves explicit integration along appropriately chosen contours in the complex plane. The care which must be taken in choosing the contour makes the way in which this "complex plane" quadrature method is applied somewhat potential dependent, but once the contour is chosen the calculations are essentially the same for all orders. This property makes the method much more convenient to use for very high order calculations on analytic model potentials. The "complex plane" quadrature method was therefore used to obtain the phase-integral results presented below. However, in other contexts, the potential independence and ease of programming of the "real line" quadrature methods of Refs. 11–14 make them particularly useful in low orders.

In both first- and higher-order approximations, inclusion of the phase correction $\sigma(E)$ is essential for cancelling the divergence of the integral $\alpha(E)$ at a potential maximum.[7,9,20] The comparison equation technique has yielded explicit expressions for the first three contributions to $\sigma(E)$, $\sigma^{(1)}$, $\sigma^{(3)}$, $\sigma^{(5)}$, in terms of the barrier integral $K(E)$ and its components [see e.g., Eqs. (10) of Ref. 9].

III. EIGENVALUES OF A SYMMETRIC DOUBLE MINIMUM POTENTIAL

As in previous studies,[7–9] we use here as an illustrative example a potential consisting of a harmonic oscillator with a Gaussian barrier in the middle:

$$\overline{V}(z) = z^2/2 + 9e^{-z^2} , \tag{8}$$

where the energy scaling parameter, defined as the harmonic oscillator frequency factor $\epsilon_s = h\nu_0$, combines with appropriate mass and length scaling parameters to yield a dimensionless potential strength parameter of $B_z = 2$. The present improved (relative to Ref. 16) quantum mechanical eigenvalues for the first 32 levels of this system are listed in Table I; they were obtained using a numerical integration mesh of $\Delta z = 0.001$ and are believed to be accurate as quoted.

TABLE I. Reduced quantum mechanical eigenvalues $\overline{E}_{QM}$ of the double minimum potential of Eq. (8) for $B_z = 2$; the barrier maximum lies at $\overline{E} = 9$.

	Symmetric (+)	Antisymmetric (−)	Splitting
$v = 0$	3.075 394 67	3.078 507 24	0.003 112 57
1	5.138 300 28	5.164 373 05	0.026 072 77
2	6.971 396 20	7.098 397 58	0.127 001 39
3	8.576 209 68	8.967 875 86	0.391 666 17
4	10.122 338 39	10.824 216 73	0.701 878 34
5	11.829 798 66	12.695 538 86	0.865 740 20
6	13.661 905 70	14.589 715 65	0.927 809 95
7	15.551 722 65	16.504 565 98	0.952 843 33
8	17.470 536 85	18.435 544 73	0.965 007 88
9	19.406 527 61	20.378 627 97	0.972 100 36
10	21.353 993 67	22.330 819 65	0.976 825 97
11	23.309 729 41	24.289 983 70	0.980 254 29
12	25.271 720 00	26.254 596 23	0.982 876 23
13	27.238 600 83	28.223 552 17	0.984 951 35
14	29.209 399 64	30.196 033 27	0.986 633 63
15	31.183 398 32	32.171 420 76	0.988 022 44

The phase-integral eigenvalues calculated for comparison with the results in Table I are converged to at least 11 decimal places, and may be obtained on request.[21] Results were obtained in orders $2N+1 = 1$, 3, and 5 by summing $(N+1)$ terms in the sums defining each of α, K, and σ in Eq. (5) (and are referred to as "with-σ" values), and also in all orders $(2N+1)$ from 1 to 13 with $\sigma(E)$ neglected in Eq. (5) (referred to as "no-σ" values).

For the 19 lowest levels of the above potential, the errors in the phase-integral eigenvalues are plotted against the quantum number in Fig. 1. The round points joined by solid lines correspond to the no-σ eigenvalues, while the triangular points joined by dashed lines are the errors in the with-σ eigenvalues. Solid points correspond to positive discrepancies ($\overline{E}_{2N+1} > \overline{E}_{QM}$) while open points indicate that this difference is negative. The integers labeling the various curves indicate the orders $2N+1$ of the associated phase-integral results. Note that the potential barrier maximum for this system lies at the energy $\overline{E} = 9$.

The results in Fig. 1A clearly confirm the fact that inclusion of the $\sigma(E)$ corrections completely removes the difficulties associated with proximity to the barrier maximum.[9,20] The functions $\sigma^{(2n+1)}$ of Ref. 9 are based on the assumption that the classical turning points on the barrier are well isolated from other classical turning points of the system. However, when the energy levels lie far below the top of the barrier, the turning point configuration is very different from that for an isolated barrier. This is the reason that inclusion of the $\sigma^{(2n+1)}$ functions of Ref. 9 does not markedly improve the results for the very lowest levels. In any case, inclusion of the $\sigma(E)$ function clearly makes the double well phase-integral quantization condition perfectly stable near the barrier maximum, and gives the relatively low order ($2N+1 = 3$ or 5) eigenvalues an accuracy more than sufficient for most applications.

It is well known that the phase integral approximations

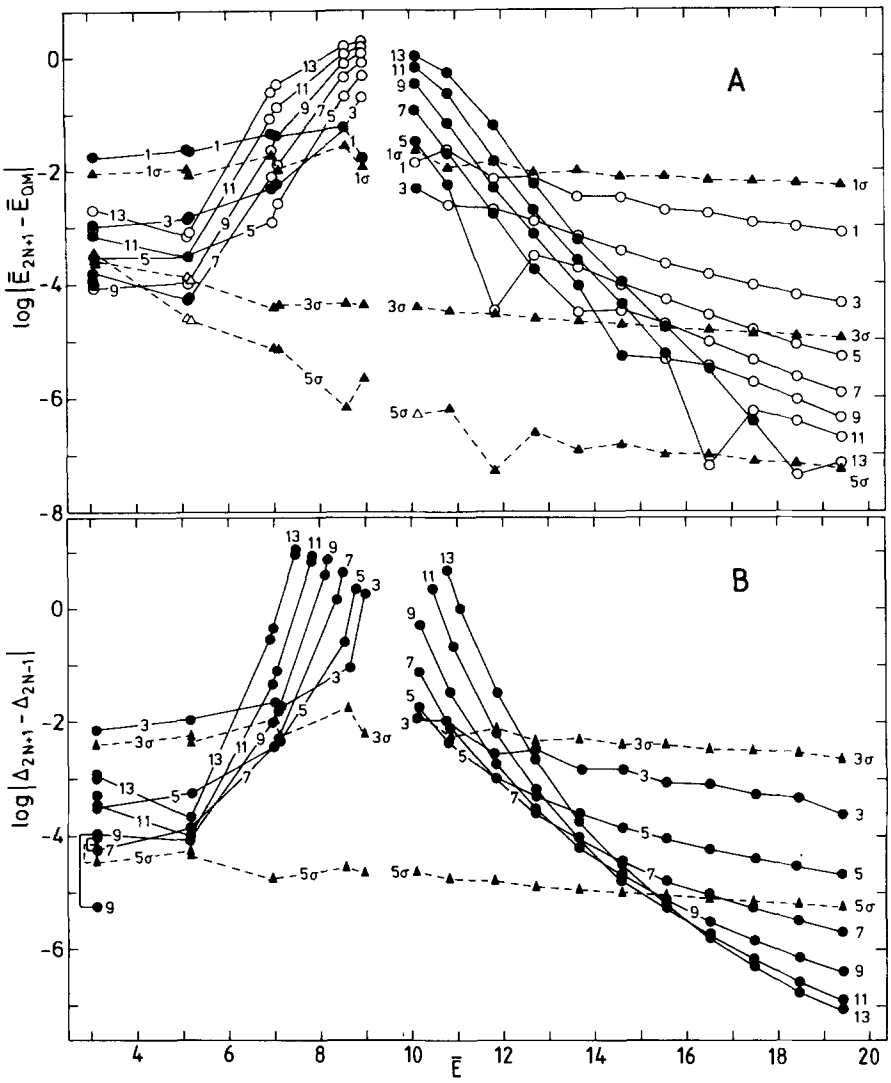

FIG. 1. (A) errors $[\bar{E}_{2N+1}-\bar{E}_{QM}]$ in $(2N+1)$th order no-σ (round points joined by solid lines) and with-σ (triangles joined by dashed lines) phase-integral eigenvalues for the $B_z=2$ reduced doubles minimum potential of Eq. (8), plotted vs the reduced energy $\bar{E}$. The integer associated with each curve is the order of approximation. Open points correspond to negative differences and solid points to positive ones. (B) The $(2N+1)$th order contributions to the right-hand side of the quantization condition (5), plotted vs the reduced energy $\bar{E}_{2N+1}$. Round points joined by solid lines correspond to no-σ calculations and triangles joined by dashed lines to with-σ results. The integer associated with each curve is the order of approximation.

are asymptotic, and the fact that the no-σ eigenvalues for a given level initially improve but eventually get worse with increasing order provides a dramatic illustration of this asymptotic nature. In the bowl of a single-minimum potential this reversal does not occur until very high orders (see Sec. IV, below). Thus, the early breakdown of the no-σ results due to the barrier maximum is particularly interesting, since it makes this behavior accessible to study. In particular, it allows us to test a simple criterion for predicting when the optimum eigenvalue for a given level has been attained and still higher-order calculations should not be trusted.

As described above, increasing the order of the phase-integral approximation applied to any given level systematically improves the calculated eigenvalue until a critical order $2N+1$ is reached, after which further increases in order make the results worse. One way of ascertaining when this optimum order has been achieved is simply to compare the magnitudes of the overall contributions to the right-hand side of the quantization condition (5) associated with each order. To this end, it is convenient to write the $(2N+1)$th order quantization condition of Eq. (5) in the form

$$v+\tfrac{1}{2}=\Delta_{2N+1}(E_{2N+1})\ . \tag{9}$$

The difference $\Delta^N\equiv|\Delta_{2N+1}(E)-\Delta_{2N-1}(E)|$ then indicates the magnitude of the net $(2N+1)$th order contribution to the phase at a given energy E. Figure 1B plots this quantity against the reduced energy $\bar{E}_{2N+1}$. Round points joined by solid lines correspond to no-σ results and triangles joined by dashed lines correspond to with-σ results. As in Fig. 1A, the integer label for each curve indicates the order of approximation. Comparison of Fig. 1A and Fig. 1B shows that minimization of Δ^N is a reasonable criterion for predicting the onset of breakdown of the high-order phase-integral approximations.

IV. EIGENVALUES OF A SINGLE MINIMUM POTENTIAL

A. Illustrative results for a model problem

Following previous work[15,17,22] the model potential used for the illustrative calculations reported here is an LJ(12, 6) function

$$\bar{V}(z)=z^{-12}-2z^{-6} \tag{10}$$

corresponding to a dimensionless well capacity parameter[15] of $B_z=10^4$ [cf. Eq. (1)], where the energy and

TABLE II. Reduced quantum mechanical eigenvalues $\bar{E}_{QM}$ and their differences with the corresponding $(2N+1)$th order phase integral eigenvalues $\bar{E}_{2N+1}$ for the 24-level LJ(12, 6) potential characterized by $B_e=10^4$.

		$10^{12}\times(\bar{E}_{2N+1}-\bar{E}_{QM})$						
v	$\bar{E}_{QM}$	$(2N+1)=1$	3	5	7	9	11	13
0	−0.941 046 032 004	−85 841 203	5118	−1	0	0	0	0
1	−0.830 002 082 986	−82 491 731	5 206	0	0	0	0	0
2	−0.727 645 697 520	−79 086 253	5 296	−1	0	0	0	0
3	−0.633 692 951 882	−75 625 016	5 391	0	0	0	0	0
4	−0.547 852 043 329	−72 108 638	5 491	0	1	1	1	1
5	−0.469 822 910 170	−68 538 172	5 599	0	1	1	1	1
6	−0.399 296 840 304	−64 915 186	5 716	0	1	1	1	1
7	−0.335 956 071 148	−61 241 847	5 848	0	1	1	1	1
8	−0.279 473 385 017	−57 521 020	5 998	0	1	1	1	1
9	−0.229 511 705 460	−53 756 368	6 174	0	1	1	1	1
10	−0.185 723 701 797	−49 952 467	6 384	0	1	1	1	1
11	−0.147 751 411 298	−46 114 913	6 640	−1	1	1	1	1
12	−0.115 225 890 999	−42 250 437	6 960	−1	1	1	1	1
13	−0.087 766 914 229	−38 367 009	7 365	−2	1	1	1	1
14	−0.064 982 730 497	−34 473 920	7 889	−3	1	1	1	1
15	−0.046 469 911 358	−30 581 835	8 579	−4	0	0	0	0
16	−0.031 813 309 316	−26 702 793	9 507	−6	1	1	1	1
17	−0.020 586 161 356	−22 850 141	10 785	−11	0	0	0	0
18	−0.012 350 373 216	−19 038 338	12 610	−18	0	0	0	0
19	−0.006 657 024 344	−15 282 616	15 351	−34	0	0	0	0
20	−0.003 047 136 244	−11 598 316	19 805	−75	−1	1	1	1
21	−0.001 052 747 695	−7 999 430	28 101	−222	−7	2	0	0
22	−0.000 198 340 301	−4 493 177	48 423	−1 235	−89	55	−16	−1
23	−0.000 002 696 883	−1 021 226	158 812	−70 317	19 692	276 925	−760 611	a

[a]In 13th order this level does not exist.

length scaling parameters ϵ_s and x_s are the depth and position of the potential minimum. One recent paper[15] reported 12 digit quantum mechanical eigenvalues for this system and compared them to first-, third-, and fifth-order phase-integral energies, while a second[22(b)] extended this comparison to seventh order. In the present work, these phase-integral results are extended to 13th order [$N=6$ in Eq. (2)].

Table II lists the quantum mechanical eigenvalues for this system [corrected according to Ref. 15(b)], together with the errors in the corresponding phase-integral energies; tabulated values of the latter, given to 13 decimal places, may be obtained on request.[21] It is interesting to note that for a number of levels these quantal eigenvalues differ slightly from the converged high-order phase-integral results. In particular, for each of $v=4$–14, 16, and 20, the phase-integral eigenvalues obtained in all orders from 9 to 13 are consistently 1×10^{-12} higher than the previously reported[15] quantal values. Since this discrepancy is orders of magnitude larger than the *differences* among the highest-order phase-integral energies of order 9–13,[21] it seems clear that it corresponds to small errors in the previously reported[15] quantal values. This observation is not surprising, since it was estimated in Ref. 15 that the errors in the latter could be as large as $\pm0.5\times10^{-12}$. However, in view of the very substantial effort which had to be expended to achieve even that degree of convergence, the existence of these small errors further illustrates the fact that extremely high accuracy is much easier to achieve using high-order phase-integral approximations rather than direct (numerical) quantum mechanical methods.

The results in Table II are consistent with the conclusion of Ref. 15 that, with the possible exception of the one level lying closest to dissociation, high-order phase-integral approximations are reliable and converge rapidly with increasing order for all levels of a realistic single minimum potential. For this model problem, the asymptotic nature of the phase-integral approximations manifest itself only for the last bound level, $v=23$, for which case the optimum result is obtained in seventh order. The manner in which the accuracy of the phase-integral eigenvalues for this level changes with increasing order is analogous to the behavior of the no-σ results in Fig. 1A for levels lying near the barrier maximum of a double minimum potential.

B. Near-dissociation behavior and breakdown of the quantization condition in high order

As was pointed out in Ref. 15, values of the $\alpha^{(2n+1)}(E)$ integrals for levels lying in the upper portion of a realistically anharmonic single minimum potential depend mainly on the nature of the integrand in the neighborhood of the outer turning point. In this long-range region, virtually all atomic and molecular interaction potentials have the limiting form

$$V(x)\simeq D-C_\nu/x^\nu\ . \tag{11}$$

As described in Ref. 15, substituting the potential approximation of Eq. (11) into Eq. (3) allows the deriva-

TABLE III. Values of the $\bar{\alpha}_\infty^{(2n+1)}(v)$ constants of Eq. (14)–(17).

v	$\bar{\alpha}_\infty^{(1)}$	$\bar{\alpha}_\infty^{(3)}$	$\bar{\alpha}_\infty^{(5)}$	$\bar{\alpha}_\infty^{(7)}$
6	−0.646 777 39	−0.204 484 89	0.098 437 50	−0.112 865 02
5	−0.835 265 19	−0.227 722 16	0.059 773 27	0.0
4	−1.198 140 23	−0.273 131 00	0.027 301 37	0.025 190 28
3	−2.240 502 60	−0.404 775 11	0.0	0.010 099 52

tion[15,23] of simple analytic expressions (identified herein by the subscript ∞) which characterize the limiting near-dissociation behavior of Eq. (3) for various values of n. In this case, Eq. (2) takes on the limiting form

$$(v+\tfrac{1}{2})^\infty = (v_D+\tfrac{1}{2}) + (1/\pi)\sum_{n=0}^{N} \bar{\alpha}_\infty^{(2n+1)}(v)/y^{n-(1/2)} , \quad (12)$$

where the independent variable is the dimensionless quantity

$$y = B_z(\bar{C}_v)^{2/v}[\bar{D}-\bar{E}]^{(v-2)/v} \quad (13)$$

and the bars on the variables C_v, D, and E indicate, as above, that energies and lengths are scaled by ϵ_s and x_s, respectively; the quantity v_D is an integration constant, which for $v>2$ is the (noninteger) first-order value of the vibrational quantum number at the dissociation limit, while the constants $\alpha_\infty^{(2n+1)}(v)$ are given by[24]

$$\bar{\alpha}_\infty^{(1)}(v) = -[1/(v-2)]\Gamma(1/2+1/v)\,\Gamma(1/2)/\Gamma(1+1/v) , \quad (14)$$

$$\bar{\alpha}_\infty^{(3)}(v) = -[(v+1)/24v]\Gamma(1/2-1/v)\,\Gamma(1/2)/\Gamma(1-1/v) , \quad (15)$$

$$\bar{\alpha}_\infty^{(5)}(v) = [(v+3)(v+1)(v-3)(2v-3)/960v^2] \times\Gamma(3/2-3/v)\,\Gamma(1/2)/\Gamma(2-3/v) , \quad (16)$$

$$\bar{\alpha}_\infty^{(7)}(v) = -[(v+5)(v+1)(v-5)(2v-5)(24v^3-22v^2-117v+139)/125152v^3]\times\Gamma(5/2-5/v)\,\Gamma(1/2)/\Gamma(3-5/v) , \quad (17)$$

where $\Gamma(a)$ is the gamma function.[25] For the values of v associated with most long-range molecular interactions, numerical values of $\alpha_\infty^{(2n+1)}(v)$ are listed in Table III.

For levels lying near dissociation, the sign of each of the higher-order (i.e., $n>0$) $\bar{\alpha}_\infty^{(2n+1)}(v)$ constants appearing in Table III is the negative of the sign of the change in the phase-integral eigenvalue when this term is added to the right-hand side of the quantization condition of Eq. (2). The fact that this sign does not simply alternate with increasing order was not evident in Ref. 15, and it explains the apparent irregularities in sign of the differences $(\bar{E}_7-\bar{E}_{QM})$ for $v=20$–23. Thus these differences do not reflect error in $\bar{E}_{QM}$ for these levels, as was suggested in Ref. 22, but merely the facts that $\bar{\alpha}_\infty^{(9)}(v=6)$ has the same signs as $\bar{\alpha}_\infty^{(7)}(v=6)$ and that for $v=23$ the optimum order is $2N+1=7$.

As was pointed out in Ref. 15, the singular behavior of the higher-order terms in Eq. (12) as $E\to D$ (i.e., as $y\to 0$) means that higher-order versions of the phase-integral quantization condition Eq. (2) breaks down for energies sufficiently near the asymptote of an interaction potential with a realistic inverse-power long-range tail. In that work,[15] a simple criterion was devised for predicting the width of the interval near dissociation where phase integral approximations of higher-order should not be used. However, the results in Table II clearly indicate that the size of the energy interval where the phase-integral eigenvalues are not very accurate depends on which order of approximation is being considered. For example, while the criterion of Ref. 15 suggests that higher-order approximations may be used for the $v=23$ level of the model LJ(12, 6) potential considered above, the results in Table II show that this is not true for orders higher than seven.

Criteria for defining the width of the breakdown interval associated with any particular order may be readily devised using Eqs. (12)–(17) and the still higher-order analogs of Eqs. (14)–(17). In particular, in the spirit of the discussion of Sec. III, a lower bound to this interval in the $(2N+1)$th order could be defined as the energy at which $|\alpha^{(2N+1)}(E)| = |\alpha^{(2N+3)}(E)|$. A more conservative criterion would be obtained on replacing the phases in this expression by their derivatives with respect to energy. This leads to the prediction that approximations of order higher than $2N+1$ should be used only when[26]

$$[\bar{D}-\bar{E}] > \left|(2N+1)\,\bar{\alpha}_\infty^{(2N+3)}/[(2N-1)\,\bar{\alpha}_\infty^{(2N+1)}\,B_z(\bar{C}_v)^{2/v}]\right|^{v/(v-2)} . \quad (18)$$

However, in most practical applications to molecular interactions, the accuracy achieved in third order is *more* than enough to account for the experimental quantities. Thus, the $N=1$ version of Eq. (18) or the generalized criterion of Eq. (29) of Ref. 15 suffices for predicting when phase-integral calculations should be restricted to first order.

C. Error estimates for phase-integral eigenvalues

Throughout the following discussion, the energy and length scaling factors ϵ_s and x_s are set equal to the depth and position of the potential minimum, so that the quantity B_z can act as a dimensionless potential strength parameter. For realistic intermolecular potentials, this definition of ϵ_s and x_s means that the magnitude of the reduced potential constant $\bar{C}_v$ [see Eq. (11)] usually lies in the range $0.2 \lesssim \bar{C}_v \lesssim 5$.[27] For reduced binding energies $[\bar{D}-\bar{E}]$ which are not too small[28] (and n values which are not too large), the Eq. (13) definition of y then shows that in the near-dissociation region, the magnitude of the $(2n+1)$th order contribution to the right-hand side of the quantization condition is largely governed by the factor $1/(B_z)^{n-(1/2)}$.

This dependence on B_z also occurs at energies far from dissociation. In particular, consideration of Eq. (3) and Eqs. (A1)–(A4) from the Appendix shows that the

$(2n+1)$th order contribution to the phase integral appearing in the quantization condition of Eq. (2) may be written as

$$\alpha^{(2n+1)}(E) = \bar{\alpha}^{(2n+1)}(\bar{E})/(B_z)^{n-(1/2)} , \tag{19}$$

where $\bar{\alpha}^{(2n+1)}(\bar{E})$ is a dimensionless contour integral depending solely on the reduced quantity $[\bar{E} - \bar{V}]$ and its derivatives with respect to z. The form of their integrands and the analogy with the near-dissociation results described above suggests that (again, except for extremely high order) at any $\bar{E}$ the values of these reduced integrals $\bar{\alpha}^{(2n+1)}(\bar{E})$ are roughly independent of n. Thus, in general the magnitudes of the higher-order contributions to phase integrals appearing in the quantization condition decrease by a factor of $1/B_z$ with each successive order.[28]

Realistic potentials which support more than one or two bound levels typically correspond to $B_z > 100$. In view of the above, the approximation

$$d(v+\tfrac{1}{2})/dE \approx (1/\pi)[d\alpha^{(1)}(E)/dE] \tag{20}$$

should be fairly accurate and a resonable estimate of the errors in the $(2N+1)$th order eigenvalues is given by

$$\delta\bar{E}_{2N+1} = -\alpha^{(2N+3)}(E)/[d\alpha^{(1)}(E)/dE]$$
$$= -\bar{\alpha}^{(2N+3)}(\bar{E})/[d\bar{\alpha}^{(1)}(\bar{E})/d\bar{E}]/(B_z)^{N+1} . \tag{21}$$

The conclusion that $\bar{\alpha}^{(2N+1)}(\bar{E})$ does not vary drastically with N then leads to the simple prediction that (for energies not too near dissociation[28]):

$$|\delta\bar{E}_{2N+1}| \approx f(\bar{E})/(B_z)^{N+1} , \tag{22}$$

where the function $f(\bar{E})$ varies slowly with energy. Equation (22) correctly predicts the magnitudes of the errors in the first-, third-, and fifth-order eigenvalues of the $B_z = 10^4$ LJ(12, 6) potential of Table II, and its utility is further confirmed by the results for the other potentials considered in Refs. 21.[28] More generally, Eqs. (21) and (22) provide a quantitative basis for the widely accepted belief that for "weaker" potentials (i.e., those corresponding to small B_z values), the phase integral quantization condition must be taken to relatively higher order for a given level of accuracy to be attained.

In the near-dissociation region, Eq. (21) takes on the limiting form

$$\delta\bar{E}^{\infty}_{2N+1} = \frac{-[2v/(v-2)]\,\bar{\alpha}^{(2N+3)}_{\infty}(v)}{\bar{\alpha}^{(1)}_{\infty}(v)\,(B_z)^{N+1}\,(\bar{C}_v)^{(n+2)/v}\,[\bar{D}-\bar{E}]^{N-2(N+1)/v}} . \tag{23}$$

For the special case of $v = 6$ long-range potentials [see Eq. (11)] for which $\bar{C}_6 = 2$, such as the family of LJ(12, 6) functions, Eq. (23), and the results in Table III yield the following error estimates for first-, third-, and fifth-order eigenvalues:

$$\delta\bar{E}^{\infty}_{1} = -0.7528\,[\bar{D}-\bar{E}]^{1/3}/B_z , \tag{24}$$

$$\delta\bar{E}^{\infty}_{3} = 0.3229/\{(B_z)^2\,[\bar{D}-\bar{E}]^{1/3}\} , \tag{25}$$

$$\delta\bar{E}^{\infty}_{5} = 0.3298/\{(B_z)^3\,[\bar{D}-\bar{E}]\} . \tag{26}$$

Figure 2 compares the predictions of Eqs. (24)–(26) (solid straight lines) with the actual eigenvalue errors for both the $B_z = 10^4$ LJ(12, 6) potential of Table II (round points) and the $B_z = 900$ LJ(12, 6) potential of Refs. 22 (triangular points).[29] The convergence of the points to the lines as $\bar{E} \to \bar{D}$ demonstrates that, as expected, the error estimates of Eqs. (23)–(26) become increasingly accurate in this limit. Moreover, the relatively small divergence of the points from these lines even at low energies demonstrates the semiquantitative validity of Eqs. (24)–(26) for *all* levels of *any* LJ(12, 6) potential. However, a more general point is illustrated by the agreement between the round and triangular points for each order. It is that, in each order, errors in the phase-integral eigenvalues of *all* potentials having the same reduced form would yield a single smooth curve on a diagram such as Fig. 2. Fitting an empirical function to this curve [preferrably one which builds in the known limiting behavior of Eq. (23)] would then yield a simple analytic estimate of the corrections required by all eigenvalues of that order for the given type of reduced potential. An approximate procedure of this type which *did not* build in the correct limiting behavior at dissociation was introduced by Cole and Tsong[30] in their study of the LJ(9, 3) potential.

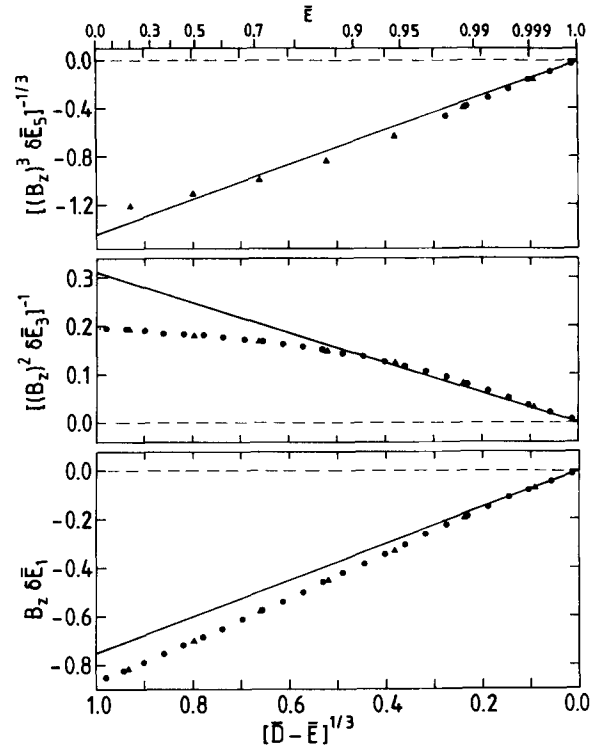

FIG. 2. Dependence of the errors $\delta\bar{E}_{2N+1}$ in the $(2N+1)$th order reduced phase-integral eigenvalues on the reduced binding energy $[\bar{D}-\bar{E}]$, for various LJ(12, 6) potentials. The straight lines correspond to the predictions of Eqs. (24)–(26) while the round points show the actual results of Table II for $B_z = 10^4$ and the triangles show the results for the $B_z = 900$ potential of Ref. 22.

V. DISCUSSION AND CONCLUSIONS

For double minimum potentials, the present study clearly demonstrates that phase-integral calculations of any order which do not incorporate the comparison equation phase correction term $\sigma(E)$ have no predictive

value close to a barrier maximum. On the other hand, proper inclusion of this correction makes the phase-integral quantization condition perfectly stable close to the barrier maximum and gives even the third or fifth order eigenvalues more than enough accuracy for most applications. Indeed, the only practical limitations on the accuracy obtainable in this way arise from the fact that σ corrections have only been derived for the first-, third-, and fifth-order phase-integral approximations.

While of little use for making practical predictions near the barrier maximum, the no-σ calculations for the double minimum potential of Eq. (8) do provide a nice illustration of the asymptotic nature of the phase-integral method. Moreover, examination of these results shows that if the magnitude of the $(2N+3)$th order contribution to the quantization condition phase at a given energy is greater than that for the $(2N+1)$th order contribution, calculations of order higher than $(2N+1)$ should not be pursued. Thus, this simple test appears to offer a reliable procedure for locating the point at which further increases in order will lead to less accurate phase-integral eigenvalues.

For realistic single minimum potentials (i.e., those having an inverse-power long-range tail), the asymptotic nature of phase-integral method appears to show itself only at energies extremely near the potential asymptote. At energies outside this region, errors in phase-integral eigenvalues decrease by a factor of roughly $1/B_z$ with each successive order, so virtually any desired accuracy can be achieved using phase-integral methods. Moreover, the simple analytic expressions which characterize the limiting near-dissociation behavior of the various contributions to the quantization condition provide a simple and reliable way of predicting the width of the region where the use of higher-order phase-integral approximations cannot be trusted. According to the analysis of Ref. 15, at most one vibrational level lies in the region near dissociation where the quantization condition cannot be used in higher order. One other general conclusion, illustrated by the results in Fig. 2, is that simple empirical expressions can be devised which accurately predict the leading higher-order corrections to the phase-integral eigenvalues of all potentials having the same reduced form.

For both single and double minimum potentials, calculations using the phase-integral method are much less expensive to perform and do not encounter the practical array size (or basis size) and integration mesh limitations which plague exact (numerical) quantal calculations at high energies or for very steep potentials. For single minimum potentials they also appear readily able to yield much higher absolute accuracy than can be practically obtained by quantal calculations using existing numerical methods, while for double minimum potentials the accuracy provided by the quantization condition in first, third, or fifth order with the σ correction included is considerably greater than is required for most purposes. Thus, for most practical purposes, the use of the phase-integral method should be thought of, not as an approximate approach to the solution of the Schrödinger equation, but rather as a particularly efficient and reliable procedure for obtaining results of virtually any desired accuracy.

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APPENDIX

Expressions for the quantities $q^{(2n+1)}(z)$ appearing in Eqs. (3) and (6) have been given earlier[3-6,18,19] for all orders of approximation of practical interest. For $n>0$ the quantities $p^{(2n+1)}(z)$, which in general are simpler than $q^{(2n+1)}(z)$, can be obtained after one or more integrations by parts. On defining $\overline{V}^l(z) \equiv d^l \overline{V}(z)/dz^l$, the first few integrands in Eqs. (3) and (6) may be written as

$$\overline{p}^{(1)}(z) = (B_z)^{1/2} [\overline{E} - \overline{V}(z)]^{1/2} , \tag{A1}$$

$$\overline{p}^{(3)}(z) = 1/[48(B_z)^{1/2}] \overline{V}^2(z)/[\overline{E} - \overline{V}(z)]^{3/2} , \tag{A2}$$

$$\overline{p}^{(5)}(z) = 1/[1536(B_z)^{3/2}] \times \{5\, \overline{V}^1(z)\, \overline{V}^3(z) - 7[\overline{V}^2(z)]^2\}/[\overline{E} - \overline{V}(z)]^{7/2} , \tag{A3}$$

$$p^{(7)}(z) = -1/[2^{16}(B_z)^{5/2}] \{5005\, [\overline{V}^1(z)]^6/[\overline{E} - \overline{V}(z)]^{17/2} - 3696\, [\overline{V}^1(z)\, \overline{V}^2(z)]^2/[\overline{E} - \overline{V}(z)]^{13/2} - 640\, [\overline{V}^2(z)]^3/[\overline{E} - \overline{V}(z)]^{11/2} + 128 [\overline{V}^3(z)]^2/[\overline{E} - \overline{V}(z)]^{9/2} . \tag{A4}$$

Note that the quantities $\overline{p}^{(2n+1)}(z)$ in Eqs. (A1)–(A4) are not unique expressions for the integrands in Eqs. (3) and (6), in the sense that the quantities of practical interest are their integrals along a closed contour, and they may be transformed into a variety of other equally correct forms by integration by parts. Expressions analogous to Eqs. (A1)–(A4) can be generated for orders higher than seven. However, the numerical evaluation of the phase integrals by explicit contour integration in the complex plane, which is the more appropriate computational method for use in such high order, does not require the integrands to be reduced to this form, so that the considerable effort required to do so was not made at this time. Unfortunately though, this prevents limiting near-dissociation behavior coefficients analogous to those of Eqs. (14)–(17) from being obtained for orders $2N+1>7$.

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[26]For the low orders $2N+1=1$ and 3, respectively, Eq. (18) is equivalent to the criteria of Eqs. (25) and (28) of Ref. 15. Of course, the accidental zeroes of $\bar{\alpha}_\infty^{(5)}(\nu=3)$ and $\bar{\alpha}_\infty^{(7)}(\nu=5)$ mean that the analogous equation for cases in which these factors would have appeared in the denominator of Eq. (18) is

$$[\bar{D}-\bar{E}]>\{|(2N+1)\bar{\alpha}_\infty^{(2N+3)}/[(2N-3)\bar{\alpha}_\infty^{(2N-1)}]|^{1/2}/B_x(\bar{C}_\nu)^{2/\nu}\}^{\nu/(\nu-2)}\ .$$

[27]For all LJ$(2\nu,\nu)$ model potentials $\bar{C}_\nu=2$.
[28]These arguments do not apply to the very narrow interval near dissociation where the high-order quantization conditions break down.
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