On the application, breakdown, and near-dissociation behavior of the higher-order JWKB quantization condition[a)]

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Numerical studies and analytic results show that singularities in the appropriate contour integrals cause the higher-order JWKB eigenvalue criteria to break down for energies near the dissociation limit of any potential with an attractive inverse power (C_n/R^n) tail for which $n > 2$. However, the expressions derived for the characteristic near-dissociation behavior of these contour integrals provide a simple way of predicting the range of binding energies over which this occurs from a knowledge of only n, the potential constant C_n, and the reduced mass μ. This analysis also shows that for more than 70% of all diatomic molecule electronic states, no vibrational levels lie in the very narrow region near dissociation where this breakdown occurs. A related near-dissociation analysis shows that for levels in the upper part of a potential well, applying the Langer–Kemble correction to the first-order quantization condition reduces the errors in calculated eigenvalues by the fraction $3/(n+1)$, for $n \geq 2$. In contrast, for the ($n=6$) model problem studied numerically, use of the two-term (third-order) or three-term (fifth-order) quantization condition reduces these errors by four or eight orders of magnitude, respectively.

I. INTRODUCTION

The Jeffries,[1] Wentzel,[2] Kramers,[3] Brillouin[4] (JWKB) "asymptotic" approximation is the most widely used approximate method for solving the one dimensional or radial Schrödinger equation. With a few exceptions[5-9] it is the single-term or first-order version of the JWKB eigenvalue criterion which has usually been used in practical applications to bound state problems. The importance of the higher-order versions of this approximation has been examined in various contexts.[9-14] However, previous methods for evaluating the higher-order terms in the eigenvalue criterion either restricted consideration to special types of potential functions, such as[10,12] the family $V(x) = x^{2m}$, or were difficult to apply accurately to a general potential function.[11]

The present work utilizes the simple and reliable quadrature procedure of Barwell and Le Roy[15] to evaluate the contour integrals appearing in the higher-order JWKB eigenvalue criteria. This removes the limitations mentioned above, since this procedure is readily applied to any smooth single minimum potential, whether it be defined by an analytic function or a set of points. Moreover, this method readily lends itself to the derivation of simple analytic expressions which accurately represent these contour integrals at energies near the dissociation limit. These expressions in turn lead to interesting conclusions regarding the reliability and importance of the higher-order JWKB eigenvalue criteria.

In Sec. II, the JWKB eigenvalue criterion is reviewed and the present method of evaluating the higher-order terms is described. The nature of the higher-order versions of this approximation is then illustrated by comparisons between the semiclassical and quantum mechanical eigenvalues of a chosen model potential.

As was found in earlier work of Beckel *et al.*,[11] the errors associated with the higher-order eigenvalue critieria increase sharply as the level energies approach the potential asymptote. The generality of this behavior is demonstrated by the analytic expressions for the characteristic "near-dissociation" (ND) behavior of the higher-order JWKB contour integrals, which are presented in Sec. IV. These expressions also yield a simple formula predicting the dominant correction to the first-order eigenvalues for levels lying near dissociation. Comparison of this result with a near-dissociation expression predicting the effect of the Langer–Kemble[16-22] correction to the JWKB approximation effectively points out the latter's lack of practical importance. Section V further examines the breakdown of the higher-order JWKB eigenvalue equations, and presents and tests simple expressions for predicting the onset of this behavior.

II. THE JWKB EIGENVALUE EQUATION

According to the JWKB approximation, the eigenvalues of a potential $V(R)$ are the energies E for which the right hand side of Eq. (1) is precisely equal to a (positive) half integer

$$v + \tfrac{1}{2} = \Delta_1 + \Delta_2 + \Delta_3 + \cdots , \tag{1}$$

where

$$\Delta_1 = \frac{1}{2\pi}\left(\frac{2\mu}{\hbar^2}\right)^{1/2} \oint [E - V(R)]^{1/2} dR , \tag{2}$$

$$\Delta_2 = \frac{1}{96\pi}\left(\frac{\hbar^2}{2\mu}\right)^{1/2} \oint \frac{V''(R)}{[E - V(R)]^{3/2}} dR , \tag{3}$$

$$\Delta_3 = \frac{1}{3072\pi}\left(\frac{\hbar^2}{2\mu}\right)^{3/2} \oint \frac{5V'(R)V'''(R) - 7[V''(R)]^2}{[E - V(R)]^{7/2}} dR . \tag{4}$$

Here, primes denote differentiation with respect to distance R, $\hbar$ is Planck's constant, and μ is the effective (reduced) mass associated with the vibration. Explicit expressions for higher-order contributions to Eq. (1) are readily obtained from the results of Fröman.[7]

It is clear from the approach of Fröman et al.[7,8] that the divers contributions to Eq. (1) are associated with the odd terms in the expansion of the wave function exponent in powers of $\hbar$, while the analogous terms for even powers of $\hbar$ define the wavefunction amplitude. Thus, the eigenvalue criteria obtained on truncating the sum in Eq. (1) at various points correspond to odd orders of the JWKB approximation. This labelling differs from the traditional identification of Δ_2 and Δ_3 as the second- and third-order,[10-13] or second- and fourth-order[5,6,9] terms. In order to minimize confusion, we shall refer to the third- and fifth-order quantization conditions obtained on truncating the sum in Eq. (1) after Δ_2 or Δ_3, as the "two-term" or "three-term" JWKB approximations, respectively.

In practical applications of Eq. (1), the first term on the right-hand side presents no difficulties, since the integrand is well behaved and the contour integral may be replaced by a line integral between the two classical turning points $R_i(E)$ [defined by $V(R_i) = E$]

$$\Delta_1 = \frac{1}{\pi}\left(\frac{2\mu}{\hbar^2}\right)^{1/2}\int_{R_1}^{R_2}[E - V(R)]^{1/2}\,dR \; . \tag{5}$$

Moreover, the apparent nonintegrable singularities in the integrands of Δ_2 and Δ_3 disappear if we write

$$\Delta_2 = -\frac{1}{24\pi}\left(\frac{\hbar^2}{2\mu}\right)^{1/2}\frac{\partial}{\partial E}\left(\int_{R_1}^{R_2}\frac{V''(R)}{[E - V(R)]^{1/2}}\,dR\right), \tag{6}$$

$$\Delta_3 = -\frac{1}{2880\pi}\left(\frac{\hbar^2}{2\mu}\right)^{3/2}\frac{\partial^3}{\partial E^3}$$

$$\times\left(\int_{R_1}^{R_2}\frac{5V'(R)V'''(R) - 7[V''(R)]^2}{[E - V(R)]^{1/2}}\,dR\right). \tag{7}$$

Defining

$$I_{k,l}^{m,n} = \frac{\partial^k}{\partial E^k}\left[\int_{R_1}^{R_2}\frac{\left(\frac{\partial^m V(R)}{\partial R^m}\right)^n}{R^l[E - V(R)]^{1/2}}\,dR\right], \tag{8}$$

then allows the quantization condition of (1) to be written as

$$v + \tfrac{1}{2} = \frac{1}{\pi}\left(\frac{2\mu}{\hbar^2}\right)^{1/2}\int_{R_1}^{R_2}(E - V)^{1/2}\,dR - \frac{1}{24\pi}\left(\frac{\hbar^2}{2\mu}\right)^{1/2}I_{1,0}^{2,1}$$

$$- \frac{1}{2880\pi}\left(\frac{\hbar^2}{2\mu}\right)^{3/2}(5I_{2,0}^{4,1} - 7I_{3,0}^{2,2}) \; . \tag{9}$$

The work of Barwell and Le Roy[15] has shown that subdividing the interval $[R_1, R_2]$ appropriately and performing integration by parts in the regions near the turning points allows one to obtain explicit expressions for the $I_{k,l}^{m,n}$ in terms of easily computed quadratures over the potential between the classical turning points. This approach, which is readily applied to either analytic or (smooth) pointwise potentials, was used in the present work.

In the usual single-term (first-order) JWKB approximation, the eigenvalues are determined from Eq. (9) with all but the first term deleted from the right-hand side. However, Langer[16] and Kemble[17] have suggested that a better result would be obtained on replacing $V(R)$ by $[V(R) + \hbar^2/8\mu R^2]$ in both the integrand and the definition of the turning points. In the following, this ap-
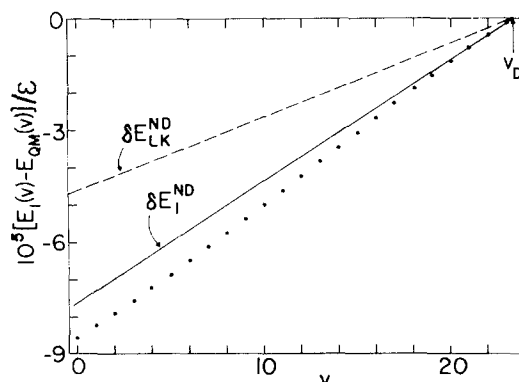

FIG. 1. Errors in single-term (first-order) JWKB eigenvalues for the $B_z = 10^4$ LJ(12, 6) potential as calculated directly (points), and as predicted by Eq. (21) (solid line) and Eq. (23) (dashed line).

proach is compared with both the normal single-term and higher-order approximations, and with quantum mechanical results.

III. NUMERICAL RESULTS FOR A MODEL POTENTIAL

In order to illustrate the nature of the higher-order JWKB approximations, detailed calculations were performed for a model potential of the LJ(12, 6) form:

$$V(R) = \epsilon\left[(R_e/R)^{12} - 2(R_e/R)^6\right] \; ,$$

where ϵ is the well depth and R_e the equilibrium distance. The well-capacity parameter[23]

$$B_z \cong 2\mu\epsilon(R_e)^2/\hbar^2$$

was chosen to be $B_z = 10^4$, so that this is the same 24-level LJ(12, 6) potential used in previous studies.[23,24] While quantum mechanical and semiclassical eigenvalues of this model potential were reported previously,[23] the present study required results of much higher accuracy. Therefore, new quantum mechanical results were generated using a program[25] based on those of Cooley[26] and Cashion.[27] These calculations were performed in double precision on a CDC-7600 computer using an integration mesh of $8\times10^{-4}R_e$ and a range of $0.5 \leqslant R/R_e \leqslant 20$,[28] and the eigenvalues obtained are believed to be accurate to ca. $\pm0.5\times10^{-12}\epsilon$. Throughout the following, energies associated with the model potential results are scaled by the well depth ϵ, and the zero of energy is set at the dissociation limit.

The quantum mechanical eigenvalues for the 24 levels of the model potential described above are presented in column 2 of Table I.[29] The remaining columns show the errors in the semiclassical eigenenergies obtained using the one-term (first-order, both with and without[29] the Langer–Kemble correction), two-term (third-order), and three-term (fifth-order) versions of the JWKB eigenvalue criterion. According to these results, the single-term and Langer–Kemble approximations are worst at the potential minimum, but become increasingly reliable for levels approaching dissociation. Indeed, a plot of the errors in the single-term eigenvalues (solid points in Fig. 1) appears to suggest (incorrectly) that

TABLE I. Quantum mechanical eigenvalues $E_{QM}(v)$ and their differences with the i term ($i = 1 - 3$) JWKB eigenvalues $E_i(v)$ for the 24-level LJ(12,6) potential defined by $B_z = 10^4$. Energies are scaled by the well depth ϵ and the zero of energy is the dissociation limit (Ref. 29).

		$10^8 \times [E_i(v) - E_{QM}(v)]$			
v	$E_{QM}(v)$	$i = 3$	2	1 (LK)[a]	1
0	− 0.941046032004	− 0.0000	0.5118	− 6122	− 8584
1	− 0.830002082986	− 0.0000	0.5206	− 5864	− 8249
2	− 0.727645697520	− 0.0000	0.5297	− 5602	− 7909
3	− 0.633692951882	− 0.0000	0.5391	− 5337	− 7562
4	− 0.547852043329	− 0.0000	0.5491	− 5068	− 7211
5	− 0.469822910710	− 0.0000	0.5598	− 4796	− 6854
6	− 0.399296840304	− 0.0000	0.5716	− 4521	− 6492
7	− 0.335956071148	− 0.0000	0.5848	− 4243	− 6124
8	− 0.279473385017	− 0.0000	0.5998	− 3963	− 5752
9	− 0.229512705496	− 0.0000	0.6173	− 3682	− 5376
10	− 0.185723701797	− 0.0000	0.6383	− 3399	− 4995
11	− 0.147751411298	− 0.0001	0.6640	− 3115	− 4611
12	− 0.115225890999	− 0.0001	0.6960	− 2832	− 4225
13	− 0.087766914229	− 0.0002	0.7365	− 2550	− 3837
14	− 0.064982730497	− 0.0003	0.7889	− 2270	− 3447
15	− 0.046469911358	− 0.0004	0.8579	− 1993	− 3058
16	− 0.031813309316	− 0.0006	0.9507	− 1721	− 2670
17	− 0.020586161356	− 0.0010	1.0785	− 1455	− 2285
18	− 0.012350373216	− 0.0018	1.2610	− 1196	− 1904
19	− 0.006657024344	− 0.0034	1.5351	− 946	− 1528
20	− 0.003047136244	− 0.0075	1.9805	− 706	− 1160
21	− 0.001052747695	− 0.0222	2.8101	− 478	− 800
22	− 0.000198340301	− 0.1234	4.8423	− 262	− 449
23	− 0.000002696883	− 7.0317	15.8813	− 53	− 102

[a]Single-term (first-order) eigenvalues obtained using the Langer−Kemble correction. (Refs. 16 and 17).

the single-term approximation becomes exact at the dissociation limit.

Table I shows that the errors in the two- and three-term JWKB eigenvalues are usually, respectively, some four and eight orders of magnitude smaller than those in the single-term eigenvalues. These errors are smallest at the potential minimum and increase in magnitude with vibrational quantum number. For the highest vibrational levels they grow particularly rapidly, and for the last bound level ($v = 23$) the two- and three-term eigenvalues are virtually no more accurate than the one-term result. This behavior appears to suggest (correctly, see below) that the higher-order JWKB approximations break down for levels lying in the immediate neighborhood of the asymptote of this type of potential.

As a check on the present procedures, it is reassuring to note that extrapolation of the one- and two-term eigenvalue discrepancies to the potential minimum yields essentially exact agreement with the zero point energy corrections $Y_{00} = 8750.0 \times 10^{-8}\epsilon$ and $Z_{00} = -0.5076 \times 10^{-8}\epsilon$ obtained from the expressions of Dunham[5] and Sandeman.[6]

The behavior of the JWKB results in Table I illustrates the fact that for LJ(12, 6) model potentials: (i) $\Delta_2(E)$ is always negative and $\Delta_3(E)$ always positive, and (ii) $|\Delta_2(E)|$ and $|\Delta_3(E)|$ both monotonically increase with energy and appear to become singular as E approaches

the dissociation limit D. The latter behavior is further illustrated in Fig. 2. For two LJ(12, 6) potentials with different well capacity parameters, the curves in this figure show the results of one-, two-, and three-term calculations of $(v + \frac{1}{2})$. By definition, the JWKB estimates of the $v = 1$ eigenvalue are the energies at which the various curves cross the horizontal line at $v + \frac{1}{2} = 1.5$. The solid points indicate the quantum mechanical energies for these two cases. It is clear that for a level sufficiently close to dissociation (e.g., $v = 1$ for $B_z = 47$), the two-term JWKB approximation will (falsely) predict it does not exist while the three-term approximation will give a worse eigenvalue than the single-term approach. It will now be demonstrated that these conclusions apply quite generally to virtually all interatomic pair potentials.

IV. NEAR-DISSOCIATION BEHAVIOR OF THE JWKB EIGENVALUE CRITERIA

A. General

In recent years it has been found that the properties of vibrational levels lying near a potential asymptote depend mainly on the long-range part of the potential energy function.[15,24,30-34] At long range, virtually all atomic and molecular interaction energies have an inverse power form,

$$V(R) \simeq D - C_n/R^n , \qquad (10)$$

and simple analytic expressions have been derived which show how the vibrational spacings,[24,30] rotational constants,[15,32] and various other properties[33,34] of levels near dissociation depend on the parameters in Eq. (10). In particular, the work of Ref. 24 showed that

$$\Delta_1^{ND}(E) = v_D + \tfrac{1}{2} - W_1(n)[D - E(v)]^{(n-2)/2n} , \quad \text{for } n \neq 2 ,$$
$$\qquad (11a)$$

$$= v_0 + \frac{1}{2} - \frac{1}{2\pi} \frac{(C_2)^{1/2}}{(\hbar^2/2\mu)^{1/2}} \ln\left(\frac{D - E(v)}{D - E(v_0)}\right) ,$$
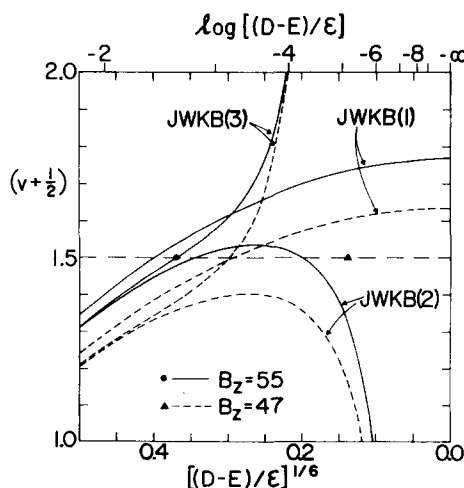$$\text{for } n = 2 . \qquad (11b)$$

FIG. 2. One-, two-, and three-term JWKB values of $(v + \frac{1}{2})$ for two model LJ(12, 6) potential functions with different well capacity parameters. The solid points denote the quantum mechanical eigenvalues for the two cases.

Here, v_D and v_0 are integration constants, and

$$W_1(n) = \left(\frac{2\mu}{\hbar^2}\right)^{1/2} \frac{(C_n)^{1/n}}{\pi(n-2)} \frac{\Gamma\left(\frac{1}{2}+\frac{1}{n}\right)\Gamma\left(\frac{1}{2}\right)}{\Gamma\left(1+\frac{1}{n}\right)}$$

$$= \overline{W}_1(n)[\,\mu^n(C_n)^2]^{1/2n} , \qquad (12)$$

where $\Gamma(x)$ is a gamma function,[35] and values of the numerical constants $\overline{W}_1(n)$ are listed in Table II.[36] For $n>2$, v_D is the effective (noninteger) vibrational quantum number at the dissociation limit, while for $n<2$ it represents the quantum defect; for $n=2$, v_0 is the quantum number of an arbitrarily chosen reference level. Equations (11) clearly show that for the $n>2$ cases which are of most physical interest, $\Delta_1(E)$ approaches a finite value as $E \to D$.

For levels near the dissociation limit D, the values of Δ_2 and Δ_3 also depend mainly on the long-range part of the potential function. Imitating the precisely analogous derivation of near-dissociation (ND) expressions for the centrifugal distortion constants[15] then yields, for $n>2$

$$\Delta_2^{ND}(E) = -W_2(n)[D - E(v)]^{-(n-2)/2n} , \qquad (13)$$

$$\Delta_3^{ND}(E) = W_3(n)[D - E]^{-3(n-2)/2n} , \qquad (14)$$

where

$$W_2(n) = \frac{\left(\frac{\hbar^2}{2\mu}\right)^{1/2}}{24\pi(C_n)^{1/n}} \left(\frac{n+1}{n}\right) \frac{\Gamma\left(\frac{1}{2}-\frac{1}{n}\right)\Gamma\left(\frac{1}{2}\right)}{\Gamma\left(1-\frac{1}{n}\right)}$$

$$= \frac{\overline{W}_2(n)}{[\,\mu^n(C_n)^2]^{1/2n}} , \qquad (15)$$

$$W_3(n) = \frac{\left(\frac{\hbar^2}{2\mu}\right)^{3/2}}{960\pi(C_n)^{3/n}} \frac{(n^2-9)(2n-3)(n+1)}{n^2}$$

$$\times \frac{\Gamma\left(\frac{3}{2}-\frac{3}{n}\right)\Gamma\left(\frac{1}{2}\right)}{\Gamma\left(2-\frac{3}{n}\right)}$$

$$= \overline{W}_3(n)/[\,\mu^n(C_n)^2]^{3/2n} , \qquad (16)$$

and values of the constants $\overline{W}_2(n)$ and $\overline{W}_3(n)$ are given in Table II. As an illustration of the applicability of these

TABLE II. Values of the numerical factors $\overline{W}_i(n) \equiv W_i(n) \times [\mu^n(C_n)^2]^{(2i-3)/2n}$ appearing in Eqs. (12), (15), and (16), calculated for masses, energies, and lengths in units $u(^{12}C = 12)$, cm^{-1}, and Å, respectively, using the physical constants of Cohen and Taylor. (Ref. 37).

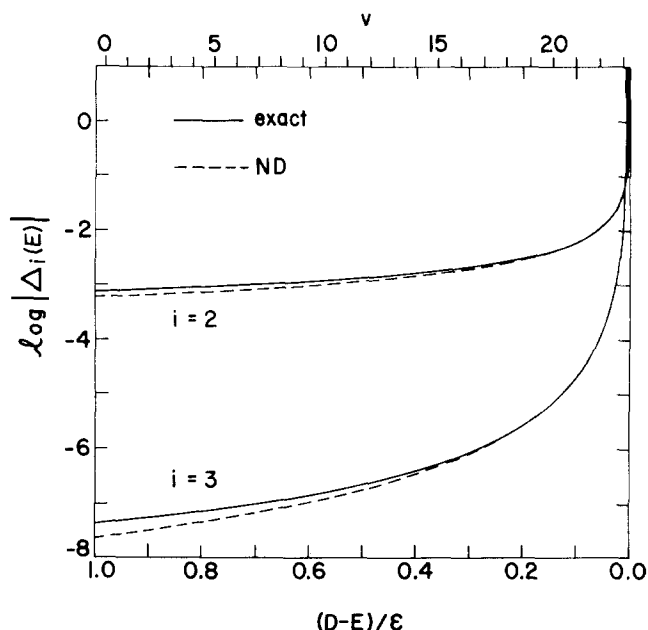| $i = 1$	2	3
$n = 3$ 0.17369900	0.5290079	0.0
4 0.09288798	0.3569599	0.6014913
5 0.06475544	0.2976142	1.3168974
6 0.05014258	0.2672450	2.1687300
8 0.03488587	0.2362136	4.2959891
10 0.02688728	0.2203793	6.9945997

FIG. 3. Comparison of ND predictions $\Delta_i^{ND}(E)$ obtained from Eqs. (13)–(16) (dashed curves) with directly calculated $\Delta_i(E)$ values (solid curves) for the $B_g = 10^4$ LJ(12, 6) model potential.

expressions, Fig. 3 shows how values of Δ_2^{ND} and Δ_3^{ND} (dashed curves) generated from Eqs. (13)–(16) approach the exact values of Δ_2 and Δ_3 (solid curves) at energies near the dissociation limit of our 24-level LJ(12, 6) model potential.

Substituting the above results into Eq. (1) yields the near-dissociation form of the three-term JWKB eigenvalue criterion:

$$(v + \tfrac{1}{2})^{ND} = (v_D + \tfrac{1}{2}) - W_1(n)(D - E)^{(n-2)/2n}$$

$$- W_2(n)[D - E]^{-(n-2)/2n}$$

$$+ W_3(n)[D - E]^{-3(n-2)/2n} . \qquad (17)$$

Differentiating this equation and inverting the result then yields the semiclassical ND expression for the vibrational frequency

$$\omega_v^{ND} \equiv \left(\frac{\partial v}{\partial E}\right)^{-1} = \left(\frac{2n}{n-2}\right)[D - E]^{(n+2)/2n} /$$

$$\left\{W_1(n) - W_2(n)[D - E]^{-(n-2)/n} + 3W_3(n)[D - E]^{-2(n-2)/n}\right\} . \qquad (18)$$

The characteristic near-dissociation behavior of this function is illustrated in Fig. 4 by plots of one-, two-, and three-term values of ω_v for the 24-level LJ(12, 6) potential ($n = 6$) considered above. Note that the singularity in $\omega_v^{ND}(2)$ seen here corresponds to a maximum in $(v + \tfrac{1}{2})_2$ of the type seen in Fig. 2.

As is well known,[38] Δ_2, Δ_3 and all higher-order JWKB terms are identically zero for an R^{-1} potential. Setting the integration constant $v_D(n = 1) = -1$ therefore makes the single-term version of Eq. (17) identical to the quantum mechanical result.

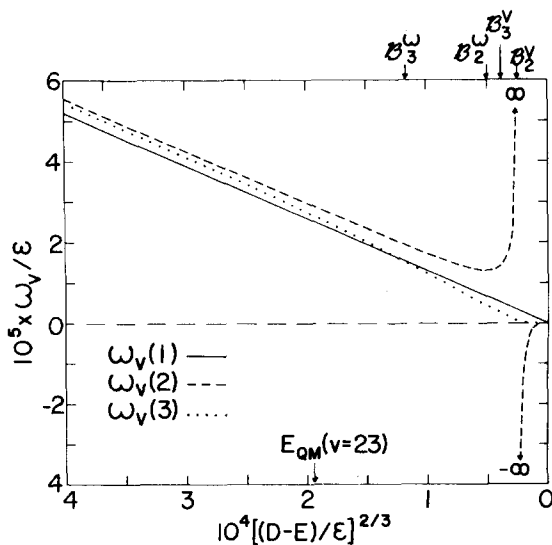For the $n = 2$ case, application of the usual ND ap-

FIG. 4. Behavior of one-, two-, and three-term values of ω_v $\equiv (dv/dE)^{-1}$ near the dissociation limit of the $B_x = 10^4$ LJ(12, 6) potential discussed in Sec. III. $E_{QM}(v = 23)$ denotes the energy of the highest bound level while the $\mathcal{B}_i^{\alpha}$ values correspond to various predictions for the onset of the breakdown of the higher-order quantization conditions (see Sec. V B).

proximations[15,24,31] to the three-term quantization condition yields

$$v + \tfrac{1}{2} = v_0 + \tfrac{1}{2} - \frac{1}{2\pi}\left(\frac{C_2}{\hbar^2/2\mu}\right)^{1/2}\left[1 - \frac{1}{2}\left(\frac{\hbar^2}{8\mu C_2}\right) - \frac{1}{8}\left(\frac{\hbar^2}{8\mu C_2}\right)^2\right]$$
$$\times \ln\left(\frac{D - E(v)}{D - E(v_0)}\right) \quad . \tag{19}$$

It is well known that for an R^{-2} potential the exact quantum mechanical eigenvalue expression is obtained by merely replacing C_2 in Eq. (11b) with $(C_2 - \hbar^2/8\mu)^{1/2}$.[38] It is therefore interesting to note that the terms due to Δ_2 and Δ_3 which distinguish Eq. (19) from the single-term result, Eq. (11b), are equal to the second and third terms in a binomial expansion of the square root of this "effective" C_2 value

$$\left(C_2 - \frac{\hbar^2}{8\mu}\right)^{1/2} = (C_2)^{1/2}\left[1 - \frac{1}{2}\left(\frac{\hbar^2}{8\mu C_2}\right)\right.$$
$$\left. - \frac{1}{8}\left(\frac{\hbar}{8\mu C_2}\right)^2 - \cdots\right] \quad .$$

This suggests that for this $(n = 2)$ case, the "asymptotic" JWKB approximation converges to the exact (quantum mechanical) result! Note, however, that the fact that $\Delta_3^{ND} \equiv 0$ for $n = 3$ [since $\overline{W}_3(3) \equiv 0$, see Table II] merely reflects the fact that $\overline{W}_3(n)$ changes sign at this value of n, and is not due to any special accuracy of the JWKB approximation for this case.

The present work focuses attention on the $n > 2$ cases for which analytic quantum mechanical results are not available. Equations (13) and (14) show that for these cases Δ_2 and Δ_3 are singular at the dissociation limit, with Δ_2 being always negative, and Δ_3 being positive for $n > 3$ and negative for $2 < n < 3$. This demonstrates the generality of the behavior of Δ_2 and Δ_3 suggested by the

numerical results in Table I and Fig. 2 (and by the work of Beckel et al.[11]). For energies sufficiently close to dissociation, the two-term eigenvalue criterion will always predict that increasing the energy further will decrease the vibrational quantum number, and that $v_D = -\infty$. For $2 < n < 3$, inclusion of Δ_3 in the quantization condition exaggerates this behavior, while for $n > 3$ the positive singularity of Δ_3 overcomes the negative singularity of Δ_2 and yields the (false) prediction that $v_D = +\infty$ for all potentials with this type of long-range tail.

These results clearly demonstrate that while inclusion of the higher-order terms significantly improves the accuracy of the JWKB eigenvalue criterion for most levels, near the dissociation limit the higher-order methods break down. However, our analytic expressions for Δ_2^{ND} and Δ_3^{ND} provide a simple means of predicting where this breakdown occurs, and also of estimating the error in single-term (first-order) JWKB eigenvalues for levels lying near dissociation. Section IV B considers the latter question and examines the importance of the Langer–Kemble correction to the single-term JWKB quantization condition.

B. Corrections to the single-term energy, and the Langer–Kemble transformation

Except for an extremely narrow region immediately below the dissociation limit (which is overlooked here) the higher-order JWKB quantum condition of Eqs. (1) and (9) yields eigenvalues which are very close to the exact (quantal) values for a given potential function. Moreover, since $|\Delta_3/\Delta_2| \ll 1$ (except for the neglected region mentioned above), the dominant source of error in the single-term (first-order) JWKB eigenvalues is due to the neglect of the term Δ_2 in Eq. (1). Thus, the errors of $\delta v \approx \Delta_2$ in the calculated values of $(v + \tfrac{1}{2})$ will give rise to errors of approximately

$$\delta E = (dE/dv) \times \delta v = \omega_v \Delta_2 , \tag{20}$$

in the single-term eigenvalues E_1. Combining the ND expressions for ω_v and Δ_2 with the single-term version of Eq. (17) then yields the result

$$\delta E_1^{ND} \equiv \omega_v^{ND}(1)\Delta_2^{ND} = -P(n)[D - E]^{2/n}$$
$$\approx -R(n)[v_D - v]^{4/(n-2)} , \tag{21}$$

where $P(n) = [2n/(n-2)]W_2(n)/W_1(n)$, and

$$R(n) = \frac{P(n)}{[W_1(n)]^{4/(n-2)}} = \frac{\overline{R}(n)}{[\mu^n(C_n)^2]^{1/(n-2)}} , \tag{22}$$

and numerical values of the constants $\overline{R}(n)$ are given in Table III. For the $(n = 6)$ $B_x = 10^4$ LJ(12, 6) potential considered in Sec. III, the solid line in Fig. 1 shows the values of δE_1^{ND} calculated from Eq. (21) [for this case, $R(6) = 3.2577 \times 10^{-6}\epsilon$]. The semiquantitative agreement with the exact discrepancies for the lowest levels (solid points in Fig. 1) is certainly a result specific to this type of simple two-term model potential. However, the accuracy of the predictions of Eq. (21) for the highest levels should hold true for all potentials with inverse power tails. Moreover, since $\omega_v(1)$ approaches zero at dissociation faster than Δ_2 blows up [cf. Eqs. (13)

TABLE III. Values of the numerical factors $\bar{R}(n)$ and $\bar{R}_{LK}(n)$ appearing in Eqs. (22) and (24), calculated using the same units and physical constants as in Table II. $f^{ND}(n)$ is the predicted fractional reduction of the error in the single-term energy, provided by the Langer–Kemble correction.

	$\bar{R}(n)$	$\bar{R}_{LK}(n)$	$f^{ND}(n)$
$n = 3$	20 073.7	15 055.2	3/4
4	1 781.56	1 068.94	3/5
5	589.144	294.572	3/6
6	318.873	136.660	3/7
8	169.118	56.373	3/9
10	124.966	34.082	3/11

and (18)], the utility of Eq. (21) is *not affected* by the singularity in Δ_2 at D.

The Langer–Kemble (LK) correction to the one-term JWKB approximation has the effect of raising the single-term eigenvalues by $B_v/4$, where B_v is the usual rotational constant associated with level v. Use of the previously reported[32] ND expression for B_v therefore yields a simple analytic expression for the LK correction to a single-term eigenvalue

$$- \delta E_{LK}^{ND} = B_v/4 = R_{LK}(n)[v_D - v]^{4/(n-2)} , \qquad (23)$$

where

$$R_{LK}(n) = \bar{R}_{LK}(n)/[\mu^n(C_n)^2]^{1/(n-2)}, \qquad (24)$$

and the numerical factors $\bar{R}_{LK}(n)$ are listed in Table III. Since Eqs. (21) and (22) and Eqs. (23) and (24) have exactly the same form, the adequacy of the LK correction in the near-dissociation region clearly depends on the agreement between $\bar{R}_{LK}(n)$ and $\bar{R}(n)$. More specifically, these expressions predict that use of the LK correction will only reduce the errors in the single-term eigenvalues by the fraction

$$f^{ND}(n) = \bar{R}_{LK}(n)/\bar{R}(n) = 3/(n+1) .$$

Comparison of the last two columns in Table I (for which case $n = 6$ and[31] $v_D = 23.358005$) shows that this prediction is fairly accurate for the highest bound levels. For this same model problem, the dashed line in Fig. 1 corresponds to δE_{LK}^{ND} values generated from Eq. (23).

The above results show that introduction of the LK correction removes only a fraction of the error in the single-term eigenvalues of levels lying near dissociation. Moreover, model calculations by Beckel *et al.*[11] on a different potential function show that inclusion of the LK correction will sometimes give *worse* results than the simple single-term method. In particular, since the LK correction always raises the energies, it will always give worse results for the lowest levels of potentials for which the Dunham constant Y_{00} is negative. Relative to the improvement obtained on using the higher-order JWKB eigenvalue criteria, the LK correction does not appear to be particularly useful.

V. BREAKDOWN OF THE HIGHER-ORDER JWKB EIGENVALUE CRITERIA

A. Near-dissociation behavior of model potential results

Quantum mechanical, and one-, two-, and three-term JWKB eigenvalues were calculated for series of LJ($2n$, n) model potentials ($n = 6$, 5, 4, and 3),

$$V(R) = \epsilon[(R_e/R)^{2n} - 2(R_e/R)^n] ,$$

corresponding to different values of the well-capacity parameter B_z. The B_z values were chosen so that the potentials had only one or two bound levels. Results for the $v = 1$ eigenvalue are presented in Figs. 5–8. The solid curves seen there represent the actual calculated energies, while the dashed curves correspond to the differences between the quantum mechanical eigenvalues E_{QM} and the i term semiclassical energies E_i. Decreasing B_z shifts the level closer to dissociation and eventually spills it out of the potential well. The arrows denoted $v_D(QM)$ and $v_D(1)$ indicate the B_z values at which the quantum mechanical and single-term
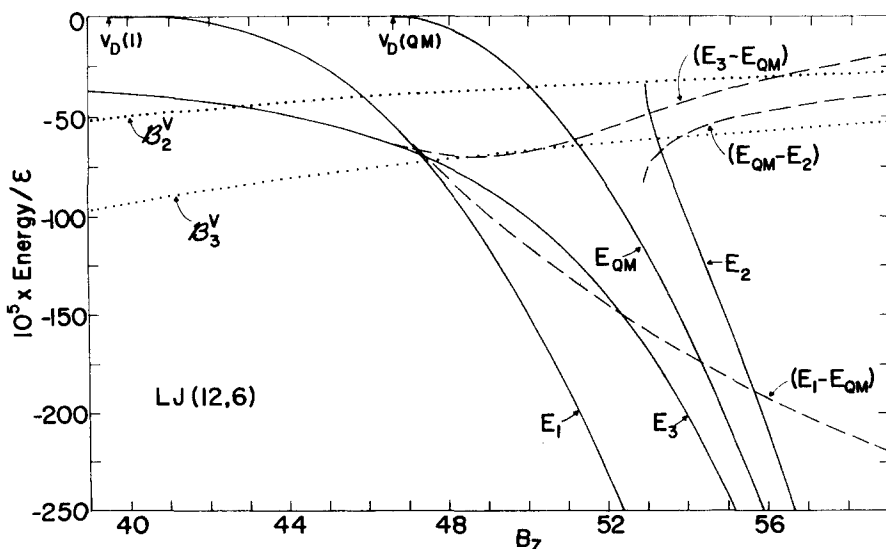

FIG. 5. Calculated eigenvalues (solid curves) and eigenvalue differences (dashed curves) of the $v = 1$ level for a series of LJ(12, 6) potentials with different well-capacity parameters. The dotted curves labelled $\mathcal{B}_i^{\alpha}$ correspond to various predictions of the onset of breakdown of the higher-order quantization conditions.
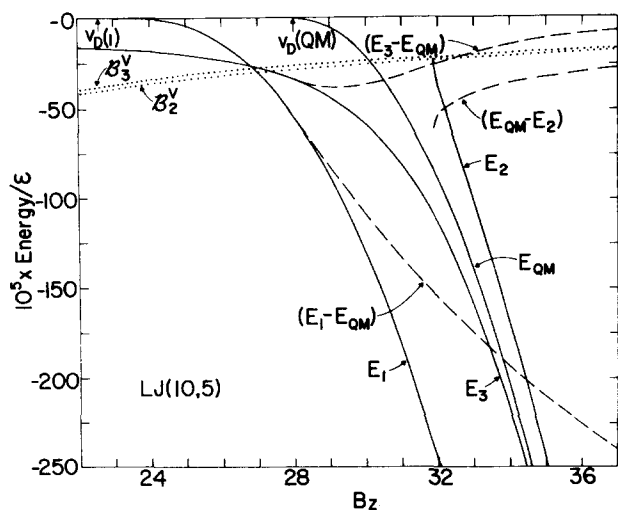
FIG. 6. For LJ(10,5) model potentials, as in Fig. 5.

JWKB eigenvalues are spilled out of the well. As was suggested by Fig. 2, the two-term JWKB eigenvalue E_2 disappears before it reaches D, at the B_z value for which the maximum in the two-term JWKB value of $(v + \frac{1}{2})$ is exactly equal to $\frac{3}{2}$ ($B_z = 53.0$ for $n = 6$). Similarly, the three-term eigenvalues E_3 remain bound for *all* nonzero B_z's.

One comforting feature of these results is the fact that up to the point at which it becomes undefined, the two-term JWKB eigenvalue provides a reasonably reliable estimate of the level energy, and the normal ordering

$$|E_1 - E_{QM}| \geq |E_2 - E_{QM}| \geq |E_3 - E_{QM}|$$

holds true. Indeed, for these $v = 1 \approx v_D$ model problems, the reversal $|E_3 - E_{QM}| > |E_1 - E_{QM}|$ usually does not occur (the exception being the LJ(12, 6) case) until the exact (quantal) eigenvalue has been spilled out of the well (see Table IV). Moreover, while large on the scale of Figs. 5–8, the largest of the $|E_2 - E_{QM}|$ and $|E_3 - E_{QM}|$ discrepancies shown here is less than 0.1% of the vibrational level spacing. However, these observations may
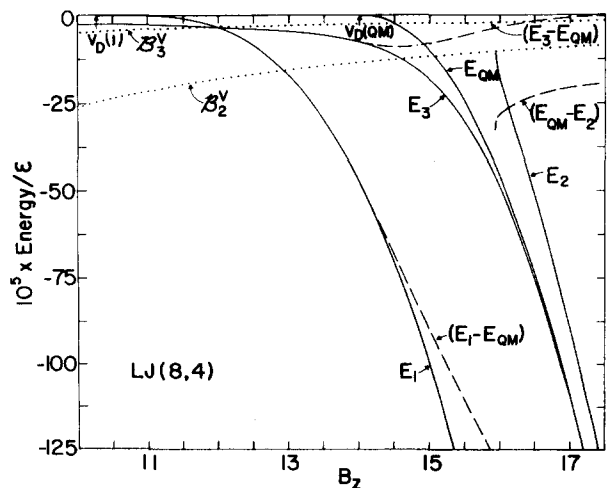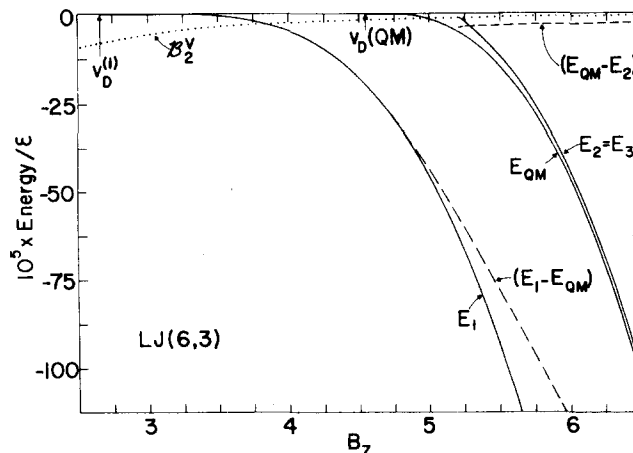

FIG. 7. For LJ(8,4) model potentials, as in Fig. 5.

FIG. 8. For LJ(6,3) model potentials, as in Fig. 5.

not generalize either to different types of potentials or to potentials having more bound levels. In addition, it is important to remember that the two-term criterion completely overlooks the existence of eigenvalue(s) lying too close to dissociation, while the three-term criterion incorrectly predicts (for $n > 3$) that an infinite number of levels lie within any finite neighborhood of D.

It is clear that the higher-order JWKB eigenvalue criteria cannot be used in the immediate neighborhood of the dissociation limit. However, the results in Figs. 5–8 show that the effect of this breakdown on the higher-order eigenvalues is not nearly as catastrophic as might be suggested by the near-dissociation behavior of the Δ_2 and Δ_3 functions, illustrated by Figs. 2 and 3. This is qualitatively explained by an argument associated with Eq. (20); the fact that $\omega_v \to 0$ for levels approaching dissociation damps the effect of the singularities in Δ_2 and Δ_3.

B. Predicting the breakdown of the higher-order JWKB eigenvalue criteria

The behavior of the curves seen in Fig. 2 points out two characteristic energies which are associated with the breakdown of the higher-order JWKB eigenvalue criteria. These are: the binding energy $\mathcal{B}_2^v$ at which the two-term result $(v + \frac{1}{2})_2$ has its maximum, and the binding energy $\mathcal{B}_3^v$ at which $(v + \frac{1}{2})_1 = (v + \frac{1}{2})_3$ (i.e., at which $\Delta_2 = \Delta_3$). An alternate perspective on this breakdown is provided by Fig. 4. The singularity in the two-

TABLE IV. For the LJ($2n, n$) potentials of Figs. 5–8, comparison of one- and three-term $v = 1$ eigenvalues at the B_z value for which the quantal value lies precisely at the dissociation limit.

n	$B_z[v_D(\text{QM}) = 1]$	E_1/ϵ	E_3/ϵ
3	4.54	0.00020	$\cdots$
4	14.00	0.00048	0.00008
5	28.02	0.00054	0.00034
6	46.62	0.00055	0.00064

TABLE V. Values of the numerical factors appearing in Eqs. (25)–(29), calculated using the same units and physical constants as in Tables II and III.

n	$\overline{K}_2^v(n)$	$\overline{K}_3^v(n)$	$\overline{K}_2^\omega(n)$	$\overline{K}_3^\omega(n)$
3	28.2484	0.0	77.5137	0.0
4	14.7679	2.8394	41.0220	25.5542
5	12.7046	11.9261	35.6482	74.4216
6	12.3042	23.1177	34.8016	120.1229
8	12.8097	47.8275	36.6525	206.9376
10	13.8685	75.3339	39.9945	297.4348

term result $\omega_v(2)$ occurs at $\mathcal{B}_2^v$, but this plot shows that $\omega_v(2)$ has unphysical behavior for binding energies less than $\mathcal{B}_2^\omega$, the point at which $\omega_v(2)$ has its minimum. Thus, the condition that $\omega_v(2)$ have zero slope (at $\mathcal{B}_2^\omega$) provides an alternate criterion for the validity of the two-term quantization condition. Similarly, the binding energy $\mathcal{B}_3^\omega$ at which $\omega_v(1) = \omega_v(3)$ provides a second possible criterion for the validity of the three-term quantization condition.

Making use of the near-dissociation expressions in Eqs. (17) and (18), expressions for these critical binding energies are readily obtained

$$\mathcal{B}_2^v = \left(\frac{W_2(n)}{W_1(n)}\right)^{n/(n-2)} = \frac{\overline{K}_2^v(n)}{[\mu^n(C_n)^2]^{1/(n-2)}} , \tag{25}$$

$$\mathcal{B}_3^v = \left(\frac{W_3(n)}{W_2(n)}\right)^{n/(n-2)} = \frac{\overline{K}_3^v(n)}{[\mu^n(C_n)^2]^{1/(n-2)}} , \tag{26}$$

$$\mathcal{B}_2^\omega = \left(\frac{3n-2}{n+2}\frac{W_2(n)}{W_1(n)}\right)^{n/(n-2)} = \frac{\overline{K}_2^\omega(n)}{[\mu^n(C_n)^2]^{1/(n-2)}} , \tag{27}$$

$$\mathcal{B}_3^\omega = \left(\frac{3W_3(n)}{W_2(n)}\right)^{n/(n-2)} = \frac{\overline{K}_3^\omega(n)}{[\mu^n(C_n)^2]^{1/(n-2)}} , \tag{28}$$

where the numerical constants $\overline{K}_2^v$, $\overline{K}_3^v$, $\overline{K}_2^\omega$, and $\overline{K}_3^\omega$ are listed in Table V. These constants show that the

ω_v criteria are distinctly more pessimistic than those based on the behavior of $(v + \frac{1}{2})$, in that the former predict breakdown of the higher-order approximations at binding energies a factor of $\gtrsim 3$ larger than do the latter. The arrows in Fig. 4 and the dotted curves in Figs. 5–8 indicate the critical binding energies predicted by these criteria. In the latter, the near coincidence of the (dotted) $\mathcal{B}_2^v$ curves with the ends of the (solid) E_2 curves, and of the (dotted) $\mathcal{B}_3^v$ curves with the intersections between the (solid) E_1 and E_3 curves demonstrates the reliability of the ND expressions of Eqs. (25)–(28).

The purpose of this section is to devise a simple criterion for predicting when the higher-order JWKB criteria should *not* be used, and for this end, the distinctions between the criteria of Eqs. (25)–(28) are not important. We therefore propose that the single equation, (29), for all $3 \le n \le 6$, be used to predict the

$$\mathcal{B}^* = 30/[\mu^n(C_n)^2]^{1/(n-2)} \tag{29}$$

smallest binding energy for which the higher-order JWKB eigenvalue criteria should be used.[39] In cases where realistic behavior of the vibrational frequency ω_v is particularly important, the numerical factor in (29) should be increased to ca. 80.

In order to demonstrate the practical significance of the breakdown of the higher-order quantization conditions, Eq. (29) has been used to predict the binding energy at which this breakdown occurs for a variety of known molecular species. The results are shown in Table VI. They suggest that at worst, only the highest bound level in a given potential will lie in the extremely narrow region near dissociation where the higher-order JWKB quantization conditions breakdown. Thus, this breakdown is of little practical concern for most problems of physical interest.

An alternate measure of the importance of this ND breakdown of the higher-order JWKB quantization con-

TABLE VI. Predicted binding energies $\mathcal{B}^*$ characterizing the breakdown of the higher-order JWKB quantization conditions, as calculated from Eq. (29). $[D - E(v_{max})]$ is the observed (predicted) binding energy of the highest bound level for each species.

Species	n	$C_n/\text{cm}^{-1}\text{Å}^n$	$[D - E(v_{max})]/\text{cm}^{-1}$	$\mathcal{B}^*/\text{cm}^{-1}$	Refs.
LJ(12,6) for $B_z = 10^4$	6	$2\epsilon R_e^6$	$2.7 \times 10^{-6}\epsilon$	$0.30 \times 10^{-6}\epsilon$	a
$D_2(X\,^1\Sigma_g^+)$	6	3.1364×10^4	1.80	0.17	40, 41
$H_2(X\,^1\Sigma_g^+)$	6	3.1407×10^4	145.6	0.47	30, 40, 42
$H_2(B\,^1\Sigma_u^+)$	3	3.6096×10^4	(0.6×10^{-7})	1.8×10^{-7}	30, 43
$Ar_2(X\,^1\Sigma_g^+)$	6	32.6×10^4	(31×10^{-4})	5.9×10^{-4}	44, 45
$HgCl(X\,^2\Sigma^+)$	6	81×10^4	b	2.1×10^{-4}	46
$HgI(X\,^2\Sigma^+)$	6	118×10^4	b	4.0×10^{-5}	46
$XeCl(X\,^2\Sigma^+)$	6	80×10^4	b	2.3×10^{-4}	47
$Cl_2(X\,^1\Sigma_g^+)$	6	46.8×10^4	b	6.0×10^{-4}	48
$Cl_2(B\,^3\Pi_{0u}^+)$	5	12.24×10^4	(1.6×10^{-2})	1.0×10^{-4}	31
$I_2(B\,^3\Pi_{0u}^+)$	5	27.76×10^4	(7.4×10^{-6})	7.0×10^{-6}	49
$CO(X\,^1\Sigma^+)$	5	9.70×10^4	b	5.7×10^{-4}	50

[a]Present work.
[b]This quantity cannot be estimated reliably since v_D is not known with sufficient accuracy.

dition is provided by the quantity Δv^*, the (semiclassical) range of v associated with the distance between the dissociation limit and the critical binding energy $\mathfrak{B}^*$ of Eq. (29). Inverting and integrating the single-term version of Eq. (18) yields an expression for Δv^* which depends *only* on the integer n, and not at all on the reduced mass μ or potential constant C_n

$$\Delta v^*(n) \equiv \int_0^{\mathfrak{B}^*} \left(\frac{\partial v}{\partial E}\right) d(D - E) = \overline{W}_1(n) \times (30)^{(n-2)/2n} \ . \quad (30)$$

The values of $\overline{W}_1(n)$ in Table I then yield $\Delta v^*(n) = 0.31$, 0.22, 0.18, and 0.16 for $n = 3, 4, 5,$ and 6, respectively. Assuming that the noninteger part of v_D is randomly distributed between zero and one, this means that for more than 70% of all molecular states,[51] *no vibrational levels* lie in the region where the higher-order JWKB quantization conditions break down, and that for all other cases only one level lies in this region.

VI. CONCLUSIONS

The present work has shown that singularities in the appropriate contour integrals cause the higher-order JWKB eigenvalue criteria to breakdown for energies near the asymptote of any potential with an attractive inverse-power (R^{-n}) potential tail for which $n > 2$. However, a near-dissociation analysis of this phenomenon has provided a simple analytic expression for predicting the range of binding energies in which this breakdown occurs. This analysis also shows that for most molecular states, no vibrational levels lie in this region. This is an important result, as it means that the great increase in accuracy provided by the higher-order JWKB approximation may be exploited with confidence for virtually all bound state problems of practical interest. Moreover, the ease with which the quadrature method of Ref. 15 yields accurate values of these higher-order contour integrals should facilitate future applications of the higher-order methods.

Another useful result concerns the importance of the Langer–Kemble correction to the ordinary single-term JWKB approximation. We found that in the near-dissociation region this correction reduces the error in the single-term eigenvalue by a factor ranging from $\frac{3}{4}$ for $n = 3$ to $\frac{5}{7}$ for $n = 6$. However, relative to the much greater improvement [by up to four orders of magnitude for our model LJ(12, 6) potential!] yielded by the higher-order JWKB approximation, this change is scarcely noticeable. Since this "correction" may even have the wrong sign for the lower vibrational levels, it appears to be of little real use in applications to the bound states of realistic potential energy functions. This conclusion should not be at all surprising, since as Pack has pointed out,[22] the Langer–Kemble transformation was introduced specifically to account for the boundary condition at the origin for $n = 2$ and 1 potentials, and there is no reason to expect it to be useful for other cases as well.

Our final point concerns the questions which might appear to be raised by the results in Figs. 5–8 regarding the reliability of the simple single-term ND expressions for the vibrational spacings[24,30] and other prop-

erties[15,31,33,34] of levels lying near dissociation. In this regard it is important to recall that in the ND analyses the quantity v_D is an unspecified integration constant which is determined in practise by fitting the single-term version of Eqs. (17) or (18) to experimental data. Thus, the essential question is really whether the single-term results correctly mimic the shape of the functional behavior of the quantum mechanical values. The model problem studies in both Ref. 24 and the present work indicate that this is true. Therefore, the simple functional behavior predicted by the single-term (first-order) ND expressions for the vibrational level distribution continues to be[31] a reliable tool for determining accurate dissociation energies and long-range potential constants.

ACKNOWLEDGMENTS

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