A two-isotope higher-order RKR-type inversion procedure

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The Rydberg–Klein–Rees (RKR) method is a valuable everyday tool for determining diatom potential energy curves. However, the RKR method is based upon the first-order WKB approximation, and while in most cases the potential curves it yields are adequate, there exist situations in which their deficiencies are unacceptable. This work addresses the above problem by presenting and testing a new higher-order, RKR-like inversion procedure which is exact within the third-order WKB approximation. The new method relies upon the existence of data for two isotopes. The turning point expressions obtained in the new method have exactly the same structure as the ordinary RKR expressions, and the procedure requires no iteration. Tests for two well-defined model problems show that the present method can yield potentials which are more accurate than those obtained from first-order RKR calculations, independent of whether or not the latter includes the widely used Kaiser correction.

I. INTRODUCTION

The Rydberg–Klein–Ress[1–3] or RKR inversion procedure of diatomic molecule spectroscopy is probably the most generally successful method for determining potential energy curves in all of molecular physics. However, the very success of this procedure has tended to cause its users to forget that it is not exact, in that it is based on the approximate first-order semiclassical (or Bohr–Sommerfeld) quantization condition. The potential energy curves it yields are sufficiently accurate for most practical purposes. However, there are situations in which their deficiencies are unacceptable. The present paper addresses this problem by presenting and testing a new higher-order RKR-type inversion procedure which is exact within the third-order phase-integral or WKB approximation.

In recent years, a number of other methods for generating "better-than-first-order-RKR" potentials have been proposed.[4–7] However, they have not been widely adopted, probably because of their relative complexity. Among other things, all of those methods are iterative, in that successive improvements to some zeroth-order potential must be calculated until a desired degree of convergence is achieved. The method proposed here is different, both in that it involves no iterations, and in that the expressions derived have exactly the same structure and are just as easy to use as those appearing in the ordinary first-order RKR procedure.

II. METHOD

A. Review of the first-order RKR method

The starting point for the ordinary first-order RKR procedure is the simple one-term WKB or Bohr–Sommerfeld quantization condition for a particle of mass μ bound by an effective one-dimensional potential $U(r)$:

$$v+\tfrac{1}{2}=(1/\pi\beta)\int_{r_1}^{r_2} dr\,[E-U(r)]^{1/2}, \tag{1}$$

where $\beta^2=(\hbar^2/2\mu)$, and $r_1(v)$ and $r_2(v)$ are the inner and outer classical turning points at the energy E, defined by the requirement that $U(r_1)=E(v)=U(r_2)$. According to this expression, the allowed eigenvalues of the system are the energies E for which the right-hand side of Eq. (1) is exactly equal to a half-integer (1/2, 3/2, 5/2, ···, etc.).

If v is treated as a continuous function of energy, then Eq. (1) may be differentiated with respect to E to obtain

$$dv/dE=(1/2\pi\beta)\int_{r_1}^{r_2} dr/[E-U(r)]^{1/2}. \tag{2}$$

This expression is proportional to that for the period of a classical oscillator moving subject to the potential $U(r)$ and following the usual manipulation of classical physics[8] it is readily inverted to yield the following expression for the width of the potential well at energy $E=E(v)$:

$$\begin{aligned} r_1(v)-r_2(v) &= 2\beta\int_0^E dE'(dv/dE')/[E-E']^{1/2} \\ &= 2\beta\int_{v_0}^{v} dv'/[E(v)-E(v')]^{1/2}, \end{aligned} \tag{3}$$

where v_0 is the value of the vibrational quantum number at the potential minimum where $E(v_0)=0$.

For a rotating system, the effective potential contains a centrifugal term

$$U(r)=U_J(r)=U_0(r)+J(J+1)\beta^2/r^2, \tag{4}$$

where J is the rotational quantum number, and the level energy depends on both v and J, $E=E(v,J)$. Differentiating Eq. (1) with respect to $[J(J+1)]$ yields

$$B(v)\frac{dv}{dE}=-(\beta/2\pi)\int_{r_1}^{r_2} dr/r^2[E-U(r)]^{1/2}, \tag{5}$$

where $B(v)=\partial E(v,J)/\partial[J(J+1)]|_{J=0}$ is the usual inertial rotational constant. Applying to Eq. (5) the same inversion procedure used on Eq. (2) then yields

$$1/r_1(v)-1/r_2(v)=(2/\beta)\int_{v_0}^{v} dv'\,B(v')/[E(v)-E(v')]^{1/2}. \tag{6}$$

Equations (3) and (6) are the usual (first-order) RKR equations for determining the classical turning points r_1 and r_2 as

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functions of the vibrational quantum number (or vibrational energy).

B. Derivation of the present third-order inversion procedure

The starting point for the present derivation is the third-order version of the semiclassical quantization condition Eq. (1):

$$v+\tfrac{1}{2}=(1/\pi\beta)\int_{r_1}^{r_2}dr[E-U(r)]^{1/2}+(\beta/96\pi)\times\oint_{\Gamma}dr\,U''(r)/[E-U(r)]^{3/2}, \tag{7}$$

where primes denote differentiation with respect to r and the contour of integration Γ encloses the portion of the real line for which $E>U(r)$.[9] It is then assumed that there exist data for two isotopic species with effective masses μ_1 and μ_2, respectively, and that the potential is exactly the same for both species. Writing out Eq. (7) for each isotope at exactly the same energy E and performing simple algebraic manipulations to cancel out the term involving the third-order phase-integral (the last term) then yields

$$[\mu_1^{1/2}(v_1+\tfrac{1}{2})-\mu_2^{1/2}(v_2+\tfrac{1}{2})](\pi\hbar/2^{1/2})/(\mu_1-\mu_2)=\int_{r_1}^{r_2}dr[E-U(r)]^{1/2}. \tag{8}$$

The right-hand side of Eq. (8) has exactly the same structure as the ordinary one-term quantization condition of Eq. (1), while the left-hand side is just a simple linear combination of the quantum numbers for the two isotopes at the given absolute energy E. Applying the same manipulations used in obtaining Eqs. (3) and (6) then yields the desired higher-order semiclassical turning point expressions:

$$r_2-r_1=[2^{1/2}\hbar/(\mu_1-\mu_2)]\int_0^E dE'\left\{\mu_1^{1/2}\frac{dv_1'}{dE'}-\mu_2^{1/2}\frac{dv_2'}{dE'}\right\}\Big/[E-E']^{1/2}$$
$$=\frac{2\beta_1}{(1-\mu_2/\mu_1)}\int_{v_0^1}^{v_1(E)}dv_1'/[E(v_1)-E(v_1')]^{1/2}-\frac{2\beta_2}{(\mu_1/\mu_2-1)}\int_{v_0^2}^{v_2(E)}dv_2'/[E(v_2)-E(v_2')]^{1/2} \tag{9}$$

and

$$1/r_1-1/r_2=[8^{1/2}/\hbar(\mu_1-\mu_2)]\int_0^E dE'\left\{\mu_1^{3/2}B_1(v_1')\frac{dv_1'}{dE'}-\mu_2^{3/2}B_2(v_2')\frac{dv_2'}{dE'}\right\}\Big/(E-E')^{1/2}$$
$$=\frac{2}{\beta_1(1-\mu_2/\mu_1)}\int_{v_0^1}^{v_1(E)}dv_1'\,B_1(v_1')/[E(v_1)-E(v_1')]^{1/2}-\frac{2}{\beta_2(\mu_1/\mu_2-1)}\int_{v_0^2}^{v_2(E)}dv_2'\,B_2(v_2')/[E(v_2)-E(v_2')]^{1/2}, \tag{10}$$

where $B_i(v_i)$ is the rotational constant for isotope i of mass μ_i. Note that in the second line of each of Eqs. (9) and (10), the values of the vibrational quantum numbers $v_1(E)$ and $v_2(E)$ which comprise the upper bounds on the integrals for the two isotopes must correspond to exactly the same absolute energy (relative to the potential minimum); i.e., $E_1[v_1(E)]=E_2[v_2(E)]$. Similarly, v_0^1 and v_0^2 correspond to the common energy of the potential minimum.

Equations (9) and (10) are our primary theoretical results. While these expressions are exact within the third-order phase-integral or WKB approximation, the integrals appearing there have the same simple structure as the integrals appearing in the ordinary first-order RKR method [see Eqs. (3) and (6)]; the integrands consist of the same singular term $[E(v)-E(v')]^{-1/2}$ multiplied by a well-behaved function of the experimental energies and $B(v)$ values. Thus, use of these expressions only involves use of the same simple numerical methods now widely used for Eqs. (3) and (6).

C. Definition and determination of the integration limits

In practice, it is usually most convenient to use the second versions of Eqs. (9) and (10) in which the integration variables are the vibrational quantum numbers for the two isotopes. The range of integration in each case runs from the potential minimum, where the vibrational quantum numbers equal v_0^1 and v_0^2, to upper limits corresponding to the same absolute energy E. Defining these upper limits simply requires one to determine the value of the second vibrational quantum number $v_2(E)$ associated with an absolute energy specified by a particular value of the first vibrational quantum number v_1. For virtually any representations of the experimental energies, this inversion of the relationship $E=E(v)$ will be quite straightforward. The only subtlety which enters the calculation is therefore the determination of $v_0^i (i=1,2)$.

Within the first-order phase-integral approximation, the fact that the integral on the right-hand side of Eq. (1) vanishes at the potential minimum means that $v_0^i=-1/2$ for all isotopes. However, the last term on the right-hand side of Eq. (7) is in general nonzero at the potential minimum, so the values of v_0^i arising in the third-order approximation generally differ from $-1/2$. The way in which v_0^i can be determined for a particular case depends on the nature of the available experimental data. However, an essential constraint which must always be satisfied is that the values of v_0 for any two isotopes (assuming they have exactly the same potential) must satisfy the relationship

$$(v_0^1+\tfrac{1}{2})/(v_0^2+\tfrac{1}{2})=(\mu_2/\mu_1)^{1/2}. \tag{11}$$

This expression arises simply from the observation that at the potential minimum, the first integral on the right-hand side of Eq. (7) vanishes, while the value of the second integral is independent of the isotope mass.

1. When both vibrational and rotational data are available

If data exist for both the rotational constants $B(v)$ and the energy levels $E(v)$, the v_0^i values may be determined in a straightforward fashion using the tools provided by Dunham.[10,11] As was pointed out by Kaiser,[12] the Dunham expression for $Y_{00} = [E(v = -\frac{1}{2}) - E(v = v_0)]$ in terms of the other vibration-rotation constants may be combined with the value of $\omega_e = dE(v)/dv|_{v=-1/2}$ to yield

$$\bar{v}_0 = -\tfrac{1}{2} - Y_{00}/\omega_e . \tag{12}$$

Equation (12) may be used to determine a value of $\bar{v}_0$ for each isotope separately. However, the stability of the present procedure requires that the values thus obtained be exactly consistent with one another in the manner specified by Eq. (11). In order to remove the effects of noise in experimental vibration-rotation constants and assure that Eq. (11) is satisfied, the desired values of $\bar{v}_0$ should be defined in terms of the appropriate mass-weighted geometric mean of the individual directly determined values of $\bar{v}_0$ [see Eq. (11)]:

$$(v_0^i + \tfrac{1}{2}) = [(\mu_1\mu_2)^{1/2}(\bar{v}_0^1 + \tfrac{1}{2})(\bar{v}_0^2 + \tfrac{1}{2})/\mu_i]^{1/2}. \tag{13}$$

2. When only vibrational data are available

If vibrational energies are known but rotational constants are not, Eq. (10) [or Eq. (6)] cannot be used, so it is impossible to determine a full potential using either the ordinary first-order RKR method or present procedure. On the other hand, data permitting, Eq. (9) [or Eq. (3)] may still be used to determine the width of the potential as a function of its depth. If some reasonable estimate can be made for the relatively steep inner wall of the potential, a realistic estimate of the overall potential energy function may thus still be obtained. The following discussion considers the question of the determination of v_0^i for such a case. However, a cautionary comment regarding the choice of such an inner wall function is presented in Sec. III C.

The absence of rotational constants also means that the Dunham constant Y_{00}, and hence the corresponding v_0^i values, cannot be determined in the straightforward manner described above. In this case, the consistency requirement of Eq. (11) is the only condition which can readily be used for determining third-order values of v_0^i. Moreover, this is only possible if the level energies for the two isotopes are accurately known relative to one another. If this is so, recalling that the vibrational quantum numbers are in general functions of energy [see Eq. (7)], the desired v_0^i values may be determined by using the (numerically inverted) energy level expressions for the two isotopes to find the absolute energy E satisfying the equation

$$[v_1(E) + \tfrac{1}{2}]/[v_2(E) + \tfrac{1}{2}] = (\mu_2/\mu_1)^{1/2}. \tag{14}$$

Within the third-order phase integral approximation, the energy thus obtained corresponds to the potential minimum, while the associated $v_i(E)$ values are the desired integration limits v_0^i.

This situation can arise in two contexts: The first is simply the case of a diatomic molecule for which the experimental data are not sufficiently extensive or well resolved to yield reliable $B(v)$ values. In this case, the experimental observables are the relative positions of the vibrational levels for the two isotopes considered separately. The only way these two vibrational ladders may be positioned correctly relative to one another is if a reliable extrapolation can be made from each data set to determine the distance to their common dissociation limit. If this can be done, Eq. (14) may be used to determine the desired integration limits and Eq. (9) used to calculate the third-order well width function implied by the given vibrational data. However, for this approach to give reliable results, the uncertainties in the extrapolations to dissociation must be much less than the associated Y_{00} values. In practice, this will very rarely be the case. For a diatomic molecule, therefore, the absence of reliable rotational constants usually precludes the application of the present third-order inversion procedure.

A second type of situation in which rotational constants are not available arises when the vibrational levels in question are the one-dimensional bound states observed in the scattering of atoms from surfaces.[13] In this case, the observable is the level binding energy itself, i.e., the distance to dissociation. The positions of the levels for the two isotopes relative to one another are therefore known, so Eq. (14) may be combined with the known level energy expressions to obtain the desired values of v_0^i, which may in turn be used in Eq. (9). An example of this type of situation is described in Sec. III C below.

III. TESTS OF THE METHOD

A. Definition of the model problems

In order to illustrate its utility, the present procedure has been applied to two model problems consisting of synthetic data generated from a known potential energy curve. In both cases, the potential used was a Lennard-Jones (12,6) function:

$$V(r) = \epsilon[(r_e/r)^6 - 1]^2. \tag{15}$$

The first model problem was defined by a well-capacity parameter[14] of $B_z = 2\mu\epsilon r_e^2/\hbar^2 = 1000$ for the light isotope and an isotopic mass ratio of exactly 2. This corresponds to a potential with (say) a well depth of $\epsilon = 1000\ \text{cm}^{-1}$, an equilibrium distance of $r_e = 4.0$ Å, and isotopic masses of $\mu_1 = 1.053\ 601\ 875$ and $\mu_2 = 2.107\ 203\ 750$ amu. For both isotopes, the Schrödinger equation was solved numerically to determine quantum mechanical level energies and rotational constants $B(v)$; the results obtained are listed in Table I. Although the calculations were significantly more accurate than this, the values used as synthetic data in the analysis described below were rounded off at the number of significant digits shown in this table.

Smooth "experimental" $E(v)$ and $B(v)$ functions were then determined by fitting the results in Table I to either the familiar Dunham[10] polynomials in $(v + \frac{1}{2})$, or to "near-dissociation expansion (NDE)" functions.[15,16] For fits of similar overall quality, the results obtained were not particularly sensitive to the form of the expansion function, as long as Eq. (13) was used to assure that Eq. (11) was satisfied. The results described below were generated using a rational fraction NDE representation[16] of the $B(v)$ values.

The second model problem again used the LJ(12,6) po-

TABLE I. Calculated vibrational level energies E_v (relative to the dissociation limit) and rotational constants B_v of the first Lennard-Jones (12,6) model problem (mass ratio = 1:2) used for testing the present method.

	$\mu_1 = 1.053\,601\,875$ amu		$\mu_2 = 2.107\,202\,75$ amu	
v	E_v (cm^{-1})	B_v (cm^{-1})	E_v (cm^{-1})	B_v (cm^{-1})
0	− 820.637	0.951 343	− 871.041	0.482 928
1	− 527.510	0.848 666	− 646.584	0.447 484
2	− 311.696	0.737 103	− 462.888	0.409 955
3	− 163.037	0.615 362	− 316.552	0.370 126
4	− 70.372 1	0.482 110	− 203.946	0.327 765
5	− 21.433 1	0.336.140	− 121.192	0.282 638
6	− 2.799 550	0.176 434	− 64.139 2	0.234 520
			− 28.353 5	0.183 216
			− 9.108 93	0.128 596
			− 1.402 75	0.070 548

tential form of Eq. (15) with $\epsilon = 1000$ cm^{-1} and $r_e = 4.0$ Å, but the reduced masses of the two isotopes were chosen to be 10 and 11 amu, respectively. The vibrational level energies calculated for these species are listed in Table II. The smooth $E(v)$ functions required by the RKR procedure were again obtained by fitting these energies to rational fraction NDE functions.[15]

B. Model problem I: An application using both vibrational and rotational data

For the first of the model problems described above ($\mu_2/\mu_1 = 2$), we used the techniques outlined in Sec. II C 1 to determine v_0^i, and then used in turn Eqs. (9) and (10), and Eqs. (3) and (6) to calculate the well width and inverse turning point difference as functions of energy. This has been done at three levels of sophistication: (i) simple first order, using Eqs. (3) and (6) with $v_0^i = -\frac{1}{2}$; (ii) Kaiser-corrected first order,[12] in which the v_0^i values used in Eqs. (3) and (6) were obtained using Eq. (12); and (iii) the present procedure based on Eqs. (12), (13), (9), and (10). Note that the first two of these approaches yield independent results for each isotope.

For each of these cases, the results obtained were compared to the well widths and inverse turning point differences of the actual model potential described above. The resulting absolute errors in the calculated quantities are shown in Figs. 1 and 2. They dramatically illustrate the improved accuracy of the present procedure relative to both the simple first-order and first-order Kaiser methods. The use of Dunham or alternate NDE functional representations of the experimental data has little effect on the behavior seen in these figures.

The error in the simple first-order method is due to its complete neglect of the second integral in the quantization condition of Eq. (7). The Kaiser approach[12] takes account of this integral, but fixes its value at that corresponding to the potential minimum. While it fares somewhat better than simple first order as far as the well width is concerned (see Fig. 1), the Kaiser approximation yields worse results for the inverse turning point difference. Thus, contrary to popular belief, use of the "Kaiser correction" does not always yield improvements on a simple first-order potential.

TABLE II. Calculated vibrational energy levels E_v (relative to the dissociation limit of the second LJ(12-6) model problem, $\mu_1/\mu_2 = 10/11$ for testing the present method.

v	$\mu_1 = 10$ amu E_v/cm^{-1}	$\mu_2 = 11$ amu E_v/cm^{-1}
0	− 939.514 930 3	− 942.281 034 1
1	− 825.772 886 2	− 833.420 389 7
2	− 721.172 367 0	− 732.889 507 6
3	− 625.405 876 4	− 640.422 550 2
4	− 538.157 132 3	− 555.746 456 9
5	− 459.100 638 2	− 478.580 604 7
6	− 387.901 240 9	− 408.636 487 0
7	− 324.213 676 5	− 345.617 308 1
8	− 267.682 111 4	− 289.217 672 5
9	− 217.939 684 0	− 239.123 198 1
10	− 174.608 058 1	− 195.010 164 5
11	− 137.296 999 0	− 156.545 170 3
12	− 105.603 987 6	− 123.384 812 4
13	− 79.113 892 7	− 95.175 402 8
14	− 57.398 725 3	− 71.552 734 9
15	− 40.017 502 1	− 52.141 920 6
16	− 26.516 255 5	− 36.557 319 1
17	− 16.428 227 5	− 24.402 584 1
18	− 9.274 294 6	− 15.270 858 9
19	− 4.563 671 7	− 8.745 152 5
20	− 1.794 949 4	− 4.398 933 8
21	− 0.457 513 5	− 1.796 980 5
22	− 0.033 410 1	− 0.496 519 1
23		− 0.048 698 5

C. Application to vibrational data alone

If data exist for the energy levels but not for the rotational constants, it is still possible to determine v_0 from the consistency requirement of Eq. (14) and then to calculate the well width function from Eq. (9). For our first model problem ($\mu_2/\mu_1 = 2.0$), comparing the errors in the results obtained in this way with those obtained using the methods

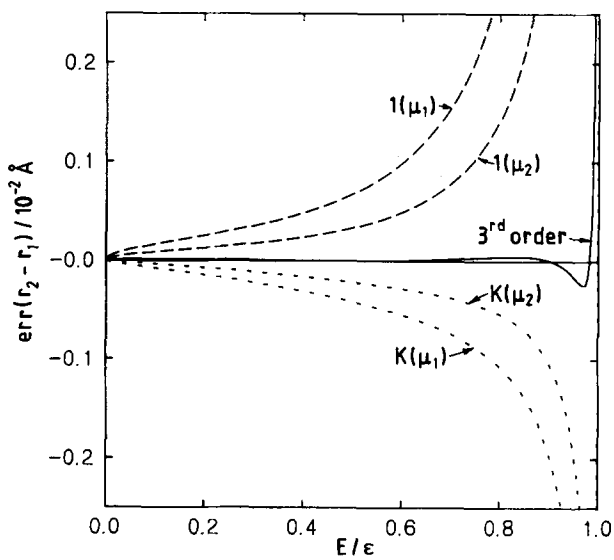

FIG. 1. For model problem I ($\mu_1/\mu_2 = 1/2$), absolute errors in calculated values of the potential width $[r_2 - r_1]$ as a function of energy E (scaled by the well depth ϵ). The solid curve represents results obtained by the present third-order method, the long-dash curves $1(\mu_1)$ and $1(\mu_2)$ the usual first-order RKR results for masses 1 and 2, respectively, and the short-dash curves $K(\mu_1)$ and $K(\mu_2)$ the corresponding Kaiser-corrected first-order results.

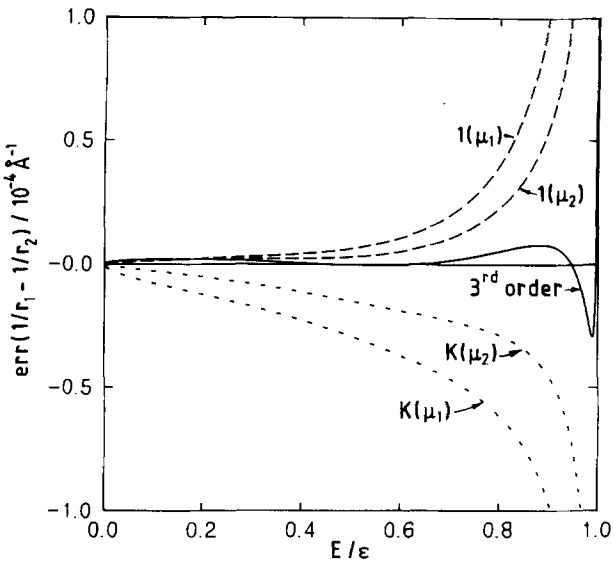

FIG. 2. For model problem I ($\mu_1/\mu_2 = 1/2$), absolute errors in the determination of $[1/r_1 - 1/r_2]$ as a function of the energy (scaled by the well depth ϵ); curves labeled the same as in Fig. 1.

discussed in Sec. II B yields results essentially identical to those shown in Fig. 1.

Another example of this type is provided by the second model problem, the one for which ($\mu_1/\mu_2 = 10/11$). Following the procedure outlined in Sec. II C 2 the energy levels were treated as if the common dissociation limit was known. Combining the resulting smooth $E(v)$ expressions with Eq. (14) yielded v_0 values for the two isotopes of $-0.500\,767\,1$ for mass 10 and $-0.500\,731\,32$ for mass 11. We note in passing that the fits imply for masses 10 and 11 a common well depth of 1000.0022 cm^{-1}; this value differs from the true value of exactly 1000.00 cm^{-1} by much less than the Y_{00} values of 0.0945 and 0.0859 cm^{-1} for isotopes of mass 10 and 11 implied by the above v_0 values. The latter values are also in good agreement with the exact value of $Y_{00} = (7/8)(\epsilon/B_z)$ for these LJ(12,6) potentials (0.0922 and 0.0838 cm^{-1}, respectively).

It has long been known that when rotational data are not available, combining a realistic extrapolation for the inner potential wall with the well width function calculated from the vibrational energies alone can give a realistic overall potential.[17–19] This is feasible because, except right near its minimum where the harmonic constant defined by the vibrational energy derivative determines its shape, the inner wall of the potential is usually sufficiently steep that virtually any plausible extrapolation will introduce little error.

Tellinghuisen and Henderson[19] recently proposed that in cases like this the inner wall of the potential be modeled by a Morse potential whose energy and shape parameters are chosen to match the first two derivatives of the vibrational energy ω_e and $\omega_e x_e$. While this is undoubtedly a good approach, it would be inappropriate to use this particular functional extrapolation in combination with a third-order well width function obtained by the present method. The reason for this is simply that for a Morse potential Y_{00} is always identically zero (i.e., $v_0 = -1/2$), which is usually inconsistent with the value of Y_{00} associated with the third order well width function. For this reason, we would recommend that the function used to represent the inner branch of the potential have derivatives at its minimum which are consistent with the derived value of Y_{00}, as well as with the experimentally obtained ω_e and $\omega_e x_e$ coefficients. The simplest way to satisfy this condition would be to use the Dunham[10] or Simons *et al.*[20] polynomial expressions for the potential, with the three leading coefficients defined by the external values of the Dunham[10] parameters Y_{00}, Y_{10}, and Y_{20}. However, any other potential form whose derivatives at the minimum satisfied this condition would be equally appropriate.

D. Numerical stability of the present procedure

The present method depends upon the existence of systematic differences between the mass-scaled properties of the two isotopes; in terms of the language introduced by Stwalley,[21] it depends on an accurate quantitative knowledge of the breakdown of the concept of mass-reduced quantum numbers. As a result, it is to be expected that it should only be used if the data in question are of fairly high quality. This question has been examined by repeating the calculations for the second model problem ($\mu_1/\mu_2 = 10/11$) using increasingly less precise input data.

In order to mimic the growth of experimental uncertainty, the number of decimal places retained in the input energy levels Table II was systematically decreased in turn from 8 to 6 to 4 to 2. In each case fits to obtain new $E(v)$ functions were performed and the resulting functions used in Eqs. (3) and (9). In these calculations, the same functional form for $E(v)$ was used for each case. For cases in which four or more decimal places were retained in the energy levels, the absolute errors in the width are virtually undistinguishable and correspond to the solid curve in Fig. 3. However, when

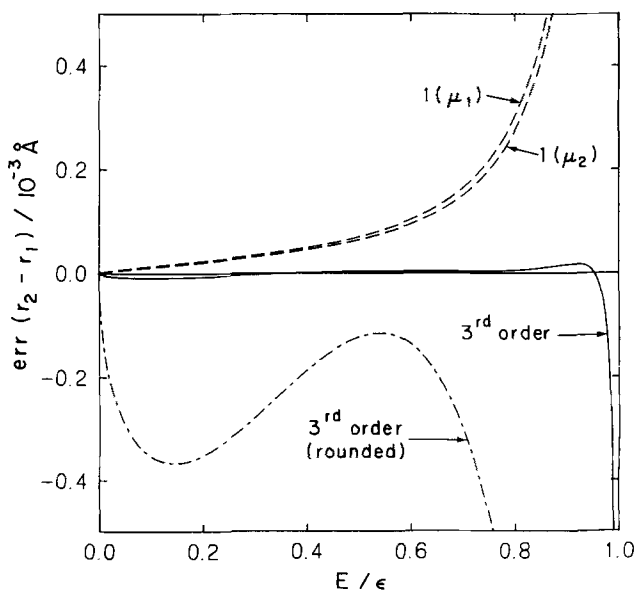

FIG. 3. For model problem II ($\mu_1/\mu_2 = 10/11$), absolute errors in the calculated values of the potential width $[r_2 - r_1]$ as a function of energy E (scaled by the well depth ϵ). The solid curve represents results obtained by the present third-order method, the long-dash curves $1(\mu_1)$ and $1(\mu_2)$ first-order RKR results for masses 10 and 11, respectively, and the long/short-dash "third-order (rounded)" curve results obtained from the present method using energies rounded off to two decimal places.

the energies are rounded off to two decimal places, the absolute errors in the width, the broken line of Fig. 3, is large. As can be seen from Fig. 3 the accuracy which can be obtained using the present method is, as expected, dependent upon the accuracy of the input energy levels. As a quantative test of the applicability of the new method we suggest the following procedure: if the standard error associated with fitting the input energy levels using mass reduced quantum numbers is larger than the standard errors associated with the fits of either isotope alone, then the present method is applicable.

IV. DISCUSSION AND CONCLUSIONS

This paper has derived and tested a method by which RKR-like turning points correct to third order may be extracted from data for two isotopes of single species. As can be seen from Figs. 1, 2, and 3, the new method yields significantly better results than either the simple first-order or Kaiser-corrected first-order RKR procedures. Moreover, the derived equations have the same simple structure as those associated with the usual first-order method and their use requires essentially the same amount of numerical effort. It was also found that use of the "Kaiser approximation" does not always yield a better overall potential than a simple first-order treatment.

For a useful application of this procedure to a real sytem, both the experimental data and its analytic representations must be of high quality and internally consistent for the two isotopes. Moreover, as the present method assumes that the two isotopes have exactly the same potential, it should not be applied unless Born–Oppenheimer breakdown effects are smaller than errors associated with use of the first-order WKB approximation.

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