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Modified semiclassical quantization conditions for double minimum potentials: Applications to anharmonic oscillators

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WKB-type connection formulas, established by Miller and Good and based on the quadratic mapping of a section of a potential containing a local minimum, are used to obtain "modified-well" quantization conditions for general double minimum potentials. Significant improvements in the usual WKB eigenvalues may be achieved by combining these with the corresponding "modified-barrier" rules. This is shown to be true in the context of the anharmonic oscillator potentials $V(x)=-kx^2+\lambda x^4$ $(k,\lambda>0)$ for a wide range of λ. The characteristic features of the different modified formalisms are also discussed.

I. INTRODUCTION

The quantum mechanics of double minimum potentials (DMP's) is a problem of recurring interest. The eigenvalue spectrum of such a potential often contains doublets of energy levels which arise when one is near "degeneracy," that is, when either well, considered independently, can support a bound state at the same energy. The semiclassical formalism is well suited for estimating such (asymptotically) degenerate energies $\bar{E}_n$ and the associated splittings Δ_n. Using established[1] WKB-type connection formulas corresponding to a quadratically mapped potential barrier, a *modified-barrier* (MB) quantization condition has been developed and applied[2,3] recently to a number of DMP's, both symmetric and asymmetric. The quantization rule for an individual well in the MB formalism differs from the usual (linear) WKB rule in that the former explicitly involves the "tunneling" integral. This, consequently, leads to more accurate values for $\bar{E}_n$ than the usual WKB results, particularly when $\bar{E}_n$ lies close to the barrier maximum.

Starting from the connection formulas[1] based on the quadratic approximation to the *well* region of a potential, we have developed in this article a *modified-well* (MW) quantization condition for a DMP. Unlike the MB formalism, the MW one gives the same value for $\bar{E}_n$ as the usual WKB method. However, the MW wave functions differ from the usual ones by an energy-dependent correction factor to the respective normalization constants.[4] This is reflected in different splittings of the level $\bar{E}_n$ from the corresponding WKB values. Taking as our clues that, as compared to the usual WKB predictions, the MB formalism leads to more accurate energies $\bar{E}_n$, while the MW rule gives better normalizations of the associated (degenerate) wave functions, these two quantization rules are combined together. In this *modified-well and barrier* (MWB) formalism, a simple expression for the doublet splittings can be written that contains the desired features of both the MB and the MW formalisms.

We have applied the above modified quantization rules to a detailed investigation of the low-lying energy levels of the double-well anharmonic oscillator potential $V(x)=-kx^2+\lambda x^4$ $(k,\lambda>0)$ for a wide range of the parameter λ. The eigenvalue structure of this potential has been studied by a variety of techniques.[5-7] Comparison with the "exact" values available in the literature[6] shows that the MWB quantization rule brings about significant improvements in the usual WKB eigenvalues. In particular, the doublet spacings are found to be fairly accurate over a wide range of magnitude. Also, since the necessary phase integrals can be obtained in simple closed form, the anharmonic oscillator problem allows a clear contrast between the MWB and WKB formalisms. Such analysis, we hope, will serve as a guide for choosing the appropriate formalism not only for the symmetric potential considered here, but for more general types of DMP's.

Several eigenvalues for a single such potential (fixed k and λ) were obtained in Ref. 3 through the MB formalism, along with results for other (asymmetric) potentials of interest in atomic and molecular physics. In contrast, the single well, or the so-called normal form of the anharmonic oscillator potential $(k<0)$ has been extensively treated through sophisticated semiclassical formalisms.[8]

II. MODIFIED QUANTIZATION RULES

Consider a particle of mass m moving in a DMP such as in Fig. 1 and an energy E corresponding to the line x_1, x_2, x_3, x_4. The WKB quantization conditions involve

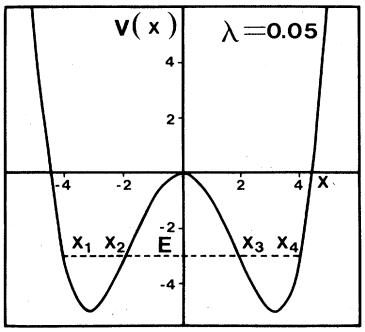

FIG. 1. Sample plot of a double-well anharmonic oscillator potential $V(x)=-x^2+\lambda x^4$. x_1, x_2, x_3, and x_4 are the classical turning points corresponding to an energy E.

the usual phase integrals over the classically "allowed" regions:

$$\alpha=\int_{x_1}^{x_2}K(x)dx,\quad \beta=\int_{x_3}^{x_4}K(x)dx, \tag{1a}$$

and the "barrier integral"

$$\phi=\int_{x_2}^{x_3}\kappa(x)dx\ , \tag{1b}$$

where

$$K(x)=\{2m[E-V(x)]/\hbar^2\}^{1/2}\equiv i\kappa(x)\ . \tag{2}$$

We would like to emphasize at this point that even though the potential in Fig. 1 is symmetric, what follows in this section is valid for asymmetric DMP's as well, so that, in general, $\alpha\neq\beta$. Applying the well-known connection formulas (based on Airy functions),[9] the usual WKB quantization condition for a DMP is easily obtained as

$$\cot\alpha\cot\beta=\tfrac{1}{4}\exp(-2\phi)\ . \tag{3}$$

Quantization for the individual wells follows, of course, from this in the limit of negligible barrier penetration, that is, $\phi\rightarrow\infty$, so that

$$\alpha=(n_\alpha+\tfrac{1}{2})\pi,\quad \beta=(n_\beta+\tfrac{1}{2})\pi,\quad n_\alpha,n_\beta=0,1,2,\ldots\ . \tag{4}$$

When both conditions (4) are satisfied at a certain energy $\overline{E}_n^{\rm WKB}$, $n=\{n_\alpha,n_\beta\}$, the resulting splitting of the level due to quantum tunneling is given in the usual WKB formalism by

$$\Delta_n^{\rm WKB}\simeq\exp(-\phi_n)\left[\left[\frac{d\alpha}{dE}\right]_{n_\alpha}\left[\frac{d\beta}{dE}\right]_{n_\beta}\right]^{-1/2}\ . \tag{5}$$

Accuracy of the above (linear) WKB expressions are known[9] to increase with the mutual separation of turning points. This, in general, implies that the phase integrals in Eq. (1) should be large. If, however, the energy E in Fig. 1 lies close to a potential extremum, say the bottom of the potential well at left, the turning points x_1 and x_2 nearly coincide and $\alpha\simeq 0$. In this case, modified WKB-type connection formulas have been established by Miller and Good[1] via the Weber-function solutions of a quadratically mapped potential that *includes* the points x_1 and x_2. Using these for the two potential wells in the method prescribed in Appendix A, we arrive at the MW quantization condition for a DMP:

$$\cot\alpha\cot\beta=\tfrac{1}{4}\exp(-2\phi)\left[\nu\left[\frac{\alpha}{\pi}\right]\nu\left[\frac{\beta}{\pi}\right]\right]\ , \tag{6}$$

where the function

$$\nu(x)\equiv[(2\pi)^{-1/2}(e/x)^x\Gamma(\tfrac{1}{2}+x)]^{-1}\ . \tag{7}$$

Note that $\nu(x)$ becomes unity when $x\rightarrow\infty$ so that the usual WKB rule (Eq. 3) is recovered when α and β become large. Also, the same quantization rules for the individual wells are obtained in this formalism: $\overline{E}_n^{\rm WKB}=\overline{E}_n^{\rm MW}$. However, the associated doublet spacings are different:

$$\Delta_n^{\rm MW}=\Delta_n^{\rm WKB}f_n\ , \tag{8}$$

where [5(c)]

$$f_n=[\nu(n_\alpha+\tfrac{1}{2})\nu(n_\beta+\tfrac{1}{2})]^{1/2}\geq 1\ . \tag{9}$$

A couple of remarks are in order here: that $\overline{E}_n^{\rm WKB}=\overline{E}_n^{\rm MW}$ is of course expected, since Eq. (6) is based on quadratic mapping of the potential wells and, as is well known, even the usual WKB rule happens to give exact results for a purely quadratic potential. However, the MW and WKB wave functions, though belonging to the same eigenvalue $\overline{E}_n$, differ in their respective normalizations. This, in essence, comes about as follows. While the usual quasiclassical wave functions are normalized in the asymptotic limit of large quantum numbers, the MW wave functions (Weber functions), being continuous at the turning points,[1] can be properly normalized[4,10] even for low quantum numbers. The MW and the WKB splittings, depending as they do on the wave functions, are therefore different. The functions ν that appear in Eq. (6) can be thus identified as the correction factors to the normalization constants of the WKB wave functions that are introduced by the MW formalism.

The MB quantization conditions, derived using the connection formulas for a parabolic potential barrier, have been discussed elsewhere.[2,3] Nevertheless, we list here the relevant expressions for completeness and for a reason that will become clear shortly. A single MB quantization condition can be used for energies both below and above the barrier maximum, say $V_{\rm max}$. Thus, if the real turning points x_2 and x_3 for $E<V_{\rm max}$ become unambiguously a pair of complex ones $x^{\pm}$ ($\mathrm{Im}x^+>0$) for $E>V_{\rm max}$ the MB quantization rule for any energy is given by

$$\cos(\tilde{\alpha}+\tilde{\beta})=-\cos(\tilde{\alpha}-\tilde{\beta}+\gamma)[1+\exp(-2\phi)]^{-1/2}\ , \tag{10}$$

where

$$\tilde{\alpha}=\alpha-\tfrac{1}{2}\mu(-\phi/\pi),\quad \tilde{\beta}=\beta-\tfrac{1}{2}\mu(-\phi/\pi)\ , \tag{11}$$

$$\gamma=\begin{cases}0, & E\leq V_{\rm max}\\ \displaystyle\int_{x^+}^{x_0}K(x)dx+\int_{x^-}^{x_0}K(x)dx, & E>V_{\rm max}\end{cases} \tag{12}$$

and

$$\mu(x)\equiv-\mu(-x)=\arg\Gamma(\tfrac{1}{2}+ix)+x(1-\ln|x|)\ . \tag{13}$$

For $E \leq V_{\max}$, α, β, and ϕ are given by (1) and for $E > V_{\max}$,

$$\alpha = \int_{x_1}^{x_0} K(x)dx, \quad \beta = \int_{x_0}^{x_4} K(x)dx, \qquad \phi = -i \int_{x_+}^{x_-} K(x)dx, \tag{14}$$

x_0 being the point where $V_{\max}$ is located. In the definition of ϕ, that branch of $K(x)$ is chosen which renders ϕ negative. For E sufficiently away from $V_{\max}$, $|\phi|$ is large, and Eq. (10) reduces to forms similar to the usual WKB expressions. Thus when $E \gg V_{\max}$, it becomes

$$\cos(\tilde{\alpha}+\tilde{\beta})=0 , \tag{15}$$

which parallels the WKB rule

$$\cos(\alpha+\beta)=0 , \tag{16}$$

and for $E \ll V_{\max}$, Eq. (10) reduces to

$$\cot\tilde{\alpha}\cot\tilde{\beta} \simeq \tfrac{1}{4}\exp(-2\phi) , \tag{17}$$

which is similar to (3). Note, however, that for ϕ large, even while terms like $\exp(-2\phi)$ can be safely ignored in Eq. (17), some coupling due to barrier penetration can still be retained via the function μ so that one gets the following MB quantization conditions for the individual potential wells:

$$\tilde{\alpha}=(n_\alpha+\tfrac{1}{2})\pi, \quad \tilde{\beta}=(n_\beta,+\tfrac{1}{2})\pi, \quad n_\alpha, n_\beta = 0,1,2,\ldots . \tag{18}$$

The expression for MB splittings, the equivalent of Eq. (5), is now given by

$$\Delta_n^{\mathrm{MB}} \simeq \exp(-\phi_n)\left[\left[\frac{d\tilde{\alpha}}{dE}\right]_{n_\alpha}\left[\frac{d\tilde{\beta}}{dE}\right]_{n_\beta}\right]^{-1/2} , \tag{19}$$

where the quantities on the right-hand side are to be evaluated at an energy $\bar{E}_n^{\mathrm{MB}}$ that satisfies conditions (18).

In view of the preceding discussions, if we note that $\bar{E}_n^{\mathrm{MB}}$ and Δ_n^{MW} represent improvements over $\bar{E}_n^{\mathrm{WKB}}$ and Δ_n^{WKB}, respectively, the MB and the MW formalisms can be combined together. Such a combination then predicts a spacing

$$\Delta_n^{\mathrm{MWB}} \simeq \Delta_n^{\mathrm{MB}} f_n \tag{20}$$

of the doublet levels around the energies $\bar{E}_n^{\mathrm{MB}}$. Note that the combined MWB formalism represents an approximation in which the potential between x_1 and x_4 is mapped onto three parabolic segments. A further approximation that underlies the expression (20) is that the exact quantal solutions (Weber functions) for each such segment are joined to those of the adjacent ones via their respective *asymptotic* expansions. A formally rigorous approach in this case would require matching the logarithmic derivatives of the solutions at the turning points that separate the segments. But in view of the surprisingly good results that we obtain in Sec. III, the MWB quantization rules [Eqs. (18) and (20)] may be of considerable practical use. An attractive feature of the simple expressions (18) and (20) is that they involve, besides the usual phase integrals,

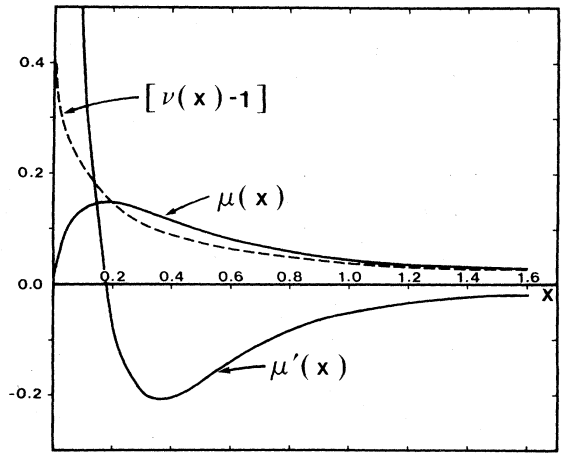

FIG. 2. Plots of the various functions required for calculating the modified semiclassical eigenvalues. $\mu(x)$ and $\nu(x)$ are given by Eqs. (13) and (7), respectively.

only the universal functions μ, μ', and ν, which can be easily calculated or read off the curves in Fig. 2.

III. APPLICATIONS

The formalism developed in the previous section is used here to obtain several eigenvalues of the double-well anharmonic oscillator Hamiltonian $H(k,\lambda)=-(d^2/dx^2) - kx^2+\lambda x^4$. All the required phase integrals (note that due to symmetry, $\alpha=\beta$) can be obtained in simple closed form involving complete elliptic integrals of the first ($\mathscr{K}$) and second ($\mathscr{E}$) kinds only and are listed in Appendix B. Evaluation of these integrals, as well as of the functions μ, is quite simple and has been done according to well-known algorithms.[11] Also, from the appropriate expansions of these functions in two distinct energy regimes, we have obtained approximate expressions for the semiclassical eigenvalues. Even though, as has been done in Sec. III B, exact numerical solutions from the different quantization conditions are straightforward to obtain, we present in Sec. III A the approximate analytical expressions for these eigenvalues.

A. Approximate eigenvalues

1. *Low-energy limit*

This limit is obtained for very low-lying doublets of energy levels around $\bar{E}_n$ and with spacings Δ_n in two deep potential wells separated by a thick barrier, and corresponds to cases when the parameter u becomes vanishingly small, where $u=(4\bar{\epsilon}_n\lambda/k^2)^{1/2}$, $\bar{\epsilon}_n=k^2/4\lambda+\bar{E}_n$. As expected from the quadratic expansions of the potential around its minima, the zeroth-order solution for $\bar{\epsilon}_n$ from the usual WKB quantization rule (4) is

$$\bar{\epsilon}_n^{(0)}=(2k)^{1/2}(2n+1) . \tag{21}$$

$u \to 0$ therefore implies that the quantity $\lambda k^{-3/2}$ is to be treated as the (small) parameter for expansion. To $O(\lambda k^{-3/2})$, Eq. (4) leads to a correction due to anharmonicity so that

$$\bar{\epsilon}_n^{\mathrm{WKB}} \simeq \epsilon_n^{(0)} \left[1 - \frac{3\sqrt{2}}{8} \lambda k^{-3/2} (2n+1) \right] \tag{22}$$

in the *usual* WKB approximation. The dominant term being of $O(\lambda^{-1}k^{3/2})$, the barrier integral ϕ is very large. Therefore, in the MWB formalism, $\bar{\epsilon}_n$ may be calculated first from Eq. (18) and, subsequently, the associated splitting can be estimated from Eq. (20). An approximate solution of Eq. (18) leads to a correction of $O(\lambda k^{-3/2})$ appearing in Eq. (22). Specifically, the MB result is

$$\bar{\epsilon}_n^{\mathrm{MB}} \simeq \bar{\epsilon}_n^{(0)} \left[1 - \frac{3\sqrt{2}}{8} \lambda k^{-3/2} (2n+1) \left[1 + \frac{1}{6(2n+1)^2} \right] \right] . \tag{23}$$

This clearly demonstrates the importance of the modified-barrier quantization rule in estimating $\bar{\epsilon}_n$. The contribution to the correction due to anharmonicity appears in the very first order in $\lambda k^{-3/2}$ and is roughly 17% for the ground-state doublets. Since $\phi \gg 1$, the splitting of the levels are exponentially small. Using Eq. (20) and keeping only the dominant terms, we obtain

$$\Delta_n^{\mathrm{MWB}} \simeq \left[\frac{k}{\pi} \right]^{1/2} \frac{2^{(10n+13)/4}}{n!} \left[\frac{k^{3/2}}{\lambda} \right]^{n+1/2} \times \exp\left[-\frac{\sqrt{2}}{3} \frac{k^{3/2}}{\lambda} \right] . \tag{24}$$

When divided by the correction factor f_n defined in Eq. (9), the above expression reduces to the WKB value and agrees with previously published results.[5(c),6] Note that as expected from the behavior of the potential as $x \to \pm\infty$, $\lambda = 0$ represents an essential singularity in the eigenvalue spectrum.

2. *High-energy limit*

This limit corresponds to energies much above the barrier maximum and to cases when $u \to \infty$. The equivalent of Eq. (21) now turns out to be

$$\epsilon_n^{(0)} = C_n^{\mathrm{WKB}} \lambda^{1/3} , \tag{25}$$

where

$$C_n^{\mathrm{WKB}} = \left[\frac{3\pi(n+\frac{1}{2})}{2\sqrt{2}\mathscr{K}(1/\sqrt{2})} \right]^{4/3} . \tag{26}$$

$\epsilon_n^{(0)}$ is the WKB eigenvalue [Eq. (16)] for the *normal* counterpart of the potential in which k is replaced by zero. Since $\epsilon_n^{(0)} \propto \lambda^{1/3}$, $u \to \infty$ implies that the expansion parameter in this case is $k\lambda^{-2/3}$. For large quantum numbers, $|\phi|$ is large, and use of Eqs. (13) and (18) leads to a correction to Eq. (25) even in the zeroth order in $k\lambda^{-2/3}$,

$$\epsilon_n^{(0)\mathrm{MB}} = C_n^{\mathrm{MB}} \lambda^{1/3} , \tag{27}$$

with

$$C_n^{\mathrm{MB}} \simeq C_n^{\mathrm{WKB}} \left[1 + \frac{1}{18\pi(n+\frac{1}{2})^2} \right] . \tag{28}$$

This correction due to the MB formalism in this order, where there is no physical potential barrier ($k=0$), is brought about by the ability of the MB formalism to handle complex turning points. The coefficients C_n^{WKB} and C_n^{MB} are compared with the corresponding numerical calculations of Chan *et al.*[12] in Table I. To first order in $k\lambda^{-2/3}$, the energy is lowered due to the additional negative term $-kx^2$ in the potential. The result is

$$\epsilon_n^{\mathrm{MB}} \simeq C_n^{\mathrm{MB}} \lambda^{1/3} \left[1 - \tfrac{1}{4} (C_n^{\mathrm{MB}})^{1/2} k \lambda^{-2/3} \times \left[\frac{\pi}{\mathscr{K}^2(1/\sqrt{2})} + \frac{1}{\sqrt{2}} \right] \right] . \tag{29}$$

The corresponding WKB expression is also given by the above with C_n^{MB} replaced by C_n^{WKB}.

It is well known[6] that through a scaling transformation the eigenvalues $E_n(k,\lambda)$ of the Hamiltonian $H(k,\lambda)$ can be mapped on to those of a reduced Hamiltonian $H(k'=1,\lambda'=\lambda k^{-3/2})$ via the relation $E_n(k,\lambda) = k^{1/2} E_n'(1,\lambda k^{-3/2})$. From the approximate expressions given in this section and the expansion parameters involved, it is easy to check that the desired scaling property of the exact eigenvalues is preserved by the semiclassical eigenvalues as well. Also, as expected from Eqs. (18) and (13), the MB formalism leads to a lowering (raising) of the corresponding WKB eigenvalues lying below (above) the barrier maximum.

TABLE I. Asymptotic behavior of the energy levels of the anharmonic oscillator in the $\lambda \to \infty$ limit. C_n^e: exact numerical result from Ref. 12; C_n^{WKB}: Eq. (26); C_n^{MB}: modified barrier, Eq. (28).

n	$\epsilon_n \propto C_n \lambda^{1/3}$ $\frac{C_n^{\mathrm{WKB}}}{C_n^e}$	$\frac{C_n^{\mathrm{MB}}}{C_n^e}$
0	0.820	0.878
1	0.990	0.998
2	0.997	1.000

B. Numerical results

As per the scaling argument stated earlier, the results shown here correspond to $k=1$ and different λ's. Also, the eigenvalues have been all shifted upward by $1/(4\lambda)$, the depth of the potential wells, to make them positive definite and amenable to ready comparison with the exact values taken from Ref. 6.

In Table II we have shown the calculated eigenvalues from the different quantization rules for sample quantum numbers of $n=0$ (the ground state) and $n=3$ for different coupling parameters λ. The $n=0$ level corresponds to the lower member of the ground pair of doublets for $\lambda \leq 0.17$, while the $n=3$ level represents the upper member of the next excited pair of doublets for $\lambda < 0.07$. For ease of comparison, we have shown in the last three columns of the table the respective differences of the different semiclassical eigenvalues from the exact ones E_n^e, listed in the second column. As expected, the MB results are found to be considerably more accurate than the others. For $n=0$, the error is less than 4%,

TABLE II. The energy levels E_n of the anharmonic oscillator potential $V(x)=-kx^2+\lambda x^4$ for sample quantum numbers $n=0$ and $n=3$. E_n^e: exact results from Ref. 6; E_n^{MW}: modified-well rule, Eq. (6); E_n^{WKB}: Eqs. (3) and (16); E_n^{MB}: modified-barrier rule, Eq. (10).

λ	E_n^e	E_n^{MW}	E_n^{WKB}	E_n^{MB}	$E_n^{MW}-E_n^e$	$E_n^{WKB}-E_n^e$	$E_n^{MB}-E_n^e$
				$n=0$			
0.03	1.3826	1.3910	1.3910	1.3863	0.0084	0.0084	0.0037
0.04	1.3711	1.3828	1.3828	1.3762	0.0117	0.0117	0.0051
0.05	1.3584	1.3738	1.3738	1.3648	0.0154	0.0154	0.0064
0.07	1.3234	1.3472	1.3479	1.3332	0.0238	0.0245	0.0098
0.10	1.2345	1.2743	1.2780	1.2519	0.0398	0.0435	0.0174
0.15	1.0625	1.1188	1.1287	1.0922	0.0563	0.0662	0.0297
0.17	1.0072	1.0628	1.0745	1.0405	0.0526	0.0673	0.0333
0.20	0.9418	0.9901	1.0039	0.9793	0.0483	0.0621	0.0375
				$n=3$			
0.03	4.0067	4.0180	4.0180	4.0106	0.0113	0.0113	0.0039
0.04	3.9183	3.9378	3.9376	3.9237	0.0195	0.0193	0.0054
0.05	3.8488	3.8889	3.8872	3.8554	0.0401	0.0384	0.0066
0.07	3.8331		3.9744	3.8400		0.1413	0.0069
0.10	4.0435		4.0639	4.0486		0.0204	0.0051
0.15	4.5898		4.5820	4.5916		−0.0078	0.0018
0.17	4.8169		4.8058	4.8176		−0.0111	0.0007
0.20	5.1483		5.1342	5.1476		−0.0141	−0.0007

while for $n=3$, they are lower than even 0.2%. The corresponding numbers for the WKB formalism are about 7% and 4%, respectively. We have noted similar improved accuracies in the MB eigenvalues for the $n=1$ and $n=2$ levels also. For a given n, the variations in error with respect to λ seem to correlate with the values of the barrier integrals involved. Notice, especially, the results for the $n=3$ level for $\lambda=0.07$, which lies slightly above the potential barrier. While the usual WKB estimate is rather poor in this case, the MB value is of quite acceptable accuracy.

Table III compares the different semiclassical predictions for the energies $\bar{E}_n$ ($n=0,1$; $n_\alpha=n_\beta=n$) around which the lowest pairs of doublets appear, with the corresponding exact values $\bar{E}_n^e$ taken from Ref. 6. For this purpose $\bar{E}_n^{WKB}$ and $\bar{E}_n^{MB}$ have been calculated from the usual [Eq. (4)] and the modified-barrier [Eq. (18)] quantization rules, respectively. $\bar{E}_n^e$ represents the simple averages of the exact energies of the members of a doublet. The entries in the last column are the corresponding estimates from a recently proposed variational scheme[7] that is based on an independent minimization technique and uses trial wave functions with two parameters. For $n=0$, the MB results are seen to be, in general, more accurate than the others and except for the MB results for $\lambda \gtrsim 0.10$, they all overestimate the energies $\bar{E}_n^e$. However, for $\lambda \gtrsim 0.10$, ϕ becomes very small, and consequently, use of the simplified Eq. (18), which is derived from Eq. (10) on the assumption that $\exp(-2\phi) \ll 1$, becomes invalid. The values within brackets for $\lambda > 0.10$ are based on the averages of the exact solutions of Eq. (10) for the doublets $n=0$ which now remain above the corresponding exact results. We also note that the variational estimates are essentially the same as the WKB predictions except at large λ, when they improve slightly. For the next higher pair of doublets $n=1$, the overall improvements of the semiclassical results can be seen. Compared to these, the variational estimates seem to be rather poor.

The results of our calculations for the doublet spacings

TABLE III. Different estimates of the energies $\bar{E}_n$ around which the lowest two doublets ($n=0,1$) appear in the spectrum of anharmonic oscillator $V(x)=-kx^2+\lambda x^4$. $\bar{E}_n^e$: exact results from Ref. 6; $\bar{E}_n^{MB}$: modified-barrier rule, Eq. (18); $\bar{E}_n^{WKB}$: Eq. (4); $\bar{E}_n^v$: a recent variational calculation, Ref. 7.

λ	$\bar{E}_n^e$	$\bar{E}_n^{MB}/\bar{E}_n^e$	$\bar{E}_n^{WKB}/\bar{E}_n^e$	$\bar{E}_n^v/\bar{E}_n^e$
		$n=0$		
0.01	1.4040	1.0009	1.0019	1.0017
0.02	1.3935	1.0018	1.0039	1.0038
0.03	1.3826	1.0027	1.0061	1.0061
0.04	1.3712	1.0036	1.0085	1.0085
0.05	1.3593	1.0046	1.0113	0.0113
0.07	1.3334	1.0067	1.0180	1.0177
0.10	1.2907	1.0072	1.0302	1.0295
0.15	1.2418	0.9860 [1.0159]	1.0279	1.0251
0.17[a]	1.2357	0.9731 [1.0171]	1.0125	1.0074
		$n=1$		
0.01	4.1702	1.0003	1.0007	0.9967
0.02	4.0920	1.0006	1.0016	0.9927
0.03	4.0064	1.0010	1.0028	0.9875
0.04	3.9098	1.0014	1.0049	0.9800
0.05	3.7979	1.0010	1.0082	

[a]For $\lambda \gtrsim 0.17$, the upper member of the doublet lies above the barrier maximum in the semiclassical calculations, though its exact value is slightly less than the barrier maximum.

TABLE IV. The splittings Δ_n of the levels $\bar{E}_n$ for the anharmonic oscillators listed in Table III. Δ_n^e: exact results, Ref. 6; Δ_n^{WKB}, Eq. (5); Δ_n^{MWB}: modified well and barrier rule, Eq. (20); Δ_n^0: modified-WKB results of Ref. 6 (see text). The rest of the notations are the same as in Table III.

λ	Δ_n^e	$\frac{\Delta_n^e}{\Delta_n^{\mathrm{WKB}}}$	$\frac{\Delta_n^e}{\Delta_n^{\mathrm{MWB}}}$	$\frac{\Delta_n^e}{\Delta_n^0}$
		$n=0$		
0.02	2.107(−9)[a]	0.993	1.000	1.005
0.03	4.339(−6)	0.990	1.000	1.006
0.04	1.862(−4)	0.985	1.000	1.007
0.05	1.712(−3)	0.979	1.000	1.008
0.07	1.999(−2)	0.958	0.993	1.006
0.10	1.124(−1)	0.924	0.977	0.975
0.15	3.586(−1)	0.894	0.977 [0.985]	0.934
0.17[b]	4.571(−1)	0.940	0.943 [0.983]	0.940
		$n=1$		
0.02	4.956(−7)	0.992	1.000	
0.03	6.063(−4)	0.984	0.999	
0.04	1.690(−2)	0.969	0.998	
0.05	1.019(−1)	0.933	0.997	

[a] $x(-n) \equiv x \times 10^{-n}$.
[b] See footnote a, Table III.

Δ_n ($n=0,1$) are shown in Table IV. Δ_n^e represent the exact spacings and are taken from Ref. 6. Notice the impressive accuracy of the MWB results. The spacings for $\lambda \geq 0.15$ are, however, more inaccurate for the same reasons that make the values $\bar{E}_n^{\mathrm{MB}}$ go below $\bar{E}_n^e$ in Table III. If we use the more accurate energies from Table III we obtain the greatly improved values shown here in appropriate places within brackets. The entries in the last column for $n=0$, taken from Ref. 6, are the ratios of the exact splittings and the corresponding "modified-WKB" splittings Δ_n^0. These modified-WKB splittings, though of the same form as the MW expression (8), are somewhat misleading in that they are evaluated at the *exact* energies $\bar{E}_n^e$, instead of at corresponding semiclassical estimates. In comparison, the MWB results, based entirely within the framework of semiclassical formalisms, are seen to be much superior.

IV. CONCLUSIONS

Two main features, which distinguish the MB and the MW formalisms from the WKB method, are revealed in the present analysis. First, the MB formalism, via the function μ of the barrier integrals, represents improved coupling between the eigenstates of motion in the "isolated" potential wells. Secondly, the MW rules incorporate better normalization characteristics of these wave functions through the correction factors ν. Thus, while the WKB estimates of the (asymptotically) degenerate levels $\bar{E}_n$ are modified by the MB formalisms, the MW one improves the associated splittings, since they depend on the overlaps of the respective degenerate wave functions peaked in either well. The MWB conditions contain both of these desirable features. Note that the MWB splittings for the anharmonic oscillators are remarkably accurate over a wide range of the anharmonicity parameter which, in turn, correspond to vastly different barrier thicknesses. This, together with the fact that the functions μ and ν are not very sensitive to the details of a potential, means that the modified quantization rules are likely to be of some success for other DMP's as well. Also note that compared to the WKB method, the simple modified formalisms involve evaluation of only two extra functions μ and ν. However, the arguments of these functions being the familiar WKB phase integrals, the little extra work involved in the application of the modified formalisms may be quite justified considering the significant improvements in the estimates that are achieved.

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APPENDIX A

In order to derive the modified-well quantization condition [Eq. (6) of Sec. II], we proceed[2] by writing the WKB solutions to the relevant Schrödinger equations in the classically forbidden regions ($x \ll x_1$, $x_2 \ll x \ll x_3$, $x \gg x_4$; refer to Fig. 1) as

$$\psi_j = A_j \Phi_j^+ + B_j \Phi_j^-, \quad j=1,2,3,4 \tag{A1}$$

where

$$\Phi_j^{\pm} = |K(x)|^{-1/2} \exp\left[\mp \int_{x_j}^{x'} \kappa(x')dx'\right]. \tag{A2}$$

The notations used here are the same as in Sec. II. Using the results of Miller and Good,[1] we first obtain a convenient matrix relation that connects the amplitudes A_2 and B_2 to the right of the turning point x_2 with the corresponding amplitudes A_1 and B_1 to the left of x_1. Specifically, they gave the following asymptotic behaviors of the linearly independent pair of the exact quantal solutions $\chi_{\pm}$ corresponding to a quadratic mapping of the potential between x_1 and x_2:

$$2\nu^{-1}\left[\frac{\alpha}{\pi}\right]\cos\alpha\,\Phi_1^+ + \sin\alpha\,\Phi_1^- \underset{x \ll x_1}{\leftarrow} \chi_+ \underset{x \gg x_2}{\rightarrow} \Phi_2^+$$

and (A3)

$$\Phi_1^- \underset{x \ll x_1}{\leftarrow} \chi_- \underset{x \gg x_2}{\rightarrow} 2\nu^{-1}\left[\frac{\alpha}{\pi}\right]\cos\alpha\,\Phi_2^- + \sin\alpha\,\Phi_2^+ .$$

Obviously, the most general solution in the region $x_1 \ll x \ll x_2$ will be a linear superposition of the type $a\chi_+ + b\chi_-$ (a,b are two hitherto arbitrary constants) whose asymptotic expressions will be of the form of ψ_1 for $x \ll x_1$ and of ψ_2 for $x \gg x_2$. Use of Eqs. (A3) and (A1)

(for $j=1,2$), leads to the following matrix relation between the corresponding amplitudes:

$$\begin{bmatrix} A_2 \\ B_2 \end{bmatrix} = M(\alpha) \begin{bmatrix} A_1 \\ B_1 \end{bmatrix} , \tag{A4}$$

where

$$M(\alpha) = \begin{bmatrix} \frac{1}{2}\nu \left[\frac{\alpha}{\pi} \right] \cos\alpha & \sin\alpha \\ -\sin\alpha & 2\nu^{-1} \left[\frac{\alpha}{\pi} \right] \cos\alpha \end{bmatrix} . \tag{A5}$$

Similarly, one obtains for the potential well between x_3 and x_4,

$$\begin{bmatrix} A_4 \\ B_4 \end{bmatrix} = M(\beta) \begin{bmatrix} A_3 \\ B_3 \end{bmatrix} . \tag{A6}$$

Finally, since ψ_2 and ψ_3 represent the wave function in the same semiclassical region $x_2 \ll x \ll x_3$, the corresponding amplitudes are simply related through the barrier integral as

$$\begin{bmatrix} A_3 \\ B_3 \end{bmatrix} = L(\phi) \begin{bmatrix} A_2 \\ B_2 \end{bmatrix} , \tag{A7}$$

where

$$L(\phi) = \begin{bmatrix} e^{-\phi} & 0 \\ 0 & e^{\phi} \end{bmatrix} . \tag{A8}$$

Equations (A6) and (A7) may be combined to write

$$\begin{bmatrix} A_2 \\ B_2 \end{bmatrix} = L^{-1}(\phi) M^{-1}(\beta) \begin{bmatrix} A_4 \\ B_4 \end{bmatrix} . \tag{A9}$$

Finiteness of the wave function as $x \to \pm\infty$ implies the boundary conditions $A_1 = B_4 = 0$. When we use these in Eqs. (A9) and (A4), we obtain

$$\frac{A_2}{B_2} = \frac{1}{2}\nu \left[\frac{\alpha}{\pi} \right] \tan\alpha = 2\nu^{-1} \left[\frac{\beta}{\pi} \right] e^{2\phi} \cot\beta , \tag{A10}$$

which immediately leads to the required quantization condition (6) in Sec. II.

APPENDIX B

Here we list all the integrals required for the results in this article for the potential $V(x) = -kx^2 + \lambda x^4$. These can be obtained very simply from standard tables[13] and involve elliptic integrals of the first ($\mathscr{K}$) and second ($\mathscr{E}$) kinds. With the definitions

$$u = \left[1 + \frac{4E\lambda}{k^2} \right]^{1/2} , \tag{B1}$$

$$c = \frac{k^{3/2}}{\lambda} , \tag{B2}$$

and

$$t^2 = \begin{cases} \dfrac{1-u}{1+u}, & E \le 0 \\ \dfrac{u-1}{u+1}, & E > 0 \end{cases} \tag{B3}$$

the required integrals are

$$\alpha = \begin{cases} \dfrac{c}{3\sqrt{2}} (1+u)^{1/2} [\mathscr{E}((1-t^2)^{1/2}) \\ \qquad -(1-u)\mathscr{K}((1-t^2)^{1/2})], & E \le 0 \\ \dfrac{c}{6} u^{1/2} \left[2\mathscr{E} \left[\dfrac{1}{(1+t^2)^{1/2}} \right] \right. \\ \qquad \left. +(u-1)\mathscr{K} \left[\dfrac{1}{(1-t^2)^{1/2}} \right] \right], & E > 0 \end{cases} \tag{B4}$$

$$\gamma = 0 \quad \text{for all } E , \tag{B5}$$

$$\frac{d\alpha}{dE} = \frac{d\beta}{dE} = [2k(1+u)]^{-1/2} \mathscr{K}((1-t^2)^{1/2}), \quad E \le 0 \tag{B6}$$

$$\phi = \begin{cases} \dfrac{\sqrt{2}}{3} c (1+u)^{1/2} [\mathscr{E}(t) - u\mathscr{K}(t)], & E \le 0 \\ -\dfrac{c}{3} u^{1/2} \left[(u+1)\mathscr{K} \left[\dfrac{t}{(1+t^2)^{1/2}} \right] \right. \\ \qquad \left. -2\mathscr{E} \left[\dfrac{t}{(1+t^2)^{1/2}} \right] \right], & E > 0 \end{cases} \tag{B7}$$

and

$$\frac{d\phi}{dE} = -\sqrt{2} k^{-1/2} (1+u)^{-1/2} \mathscr{K}(t), \quad E \le 0 . \tag{B8}$$

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