Asymptotic properties of eigenvalues in variational calculations for double-well oscillators

Asymptotic properties of eigenvalues in variational calculations for double-well oscillators

V I Yukalov and E P Yukalova

Department of Mathematics and Statistics, Queen's University, Kingston, Ontario K7L 3N6, Canada and International Centre of Condensed Matter Physics, University of Brasilia, CP 04513, Brasilia 70919-970, DF, Brazil

Abstract. Simple and accurate formulae for the eigenvalues of the Hamiltonian with an anharmonic double-well potential are presented. Special attention is paid to the following three regions of coupling parameters where difficulties arise. (i) In the weak coupling limit, the eigenvalues depend on the coupling parameter nonanalytically. To obtain accurate explicit expressions in this limit, a *composite asymptotic expansion* is applied. (ii) In the strong coupling limit, the derivation of asymptotic expansions is obstructed by the nonuniqueness of solutions to variational equations. To overcome this obstacle, a *restricted variational procedure* is suggested. (iii) There exist also critical values of the coupling parameter at which eigenvalues cross zero. In the regions around these critical values a dramatic increase of the percentage error occurs. A remedy against this critical behaviour is the *positive definite shift* removing the critical regions. The formulae obtained for the eigenvalues provide an accuracy within the errors not exceeding 3% for all values of the coupling parameter, from zero to infinity.

1. Introduction

Different variational calculations are widely used in quantum mechanics, statistical mechanics and field theory. In quantum-mechanical problems, variational parameters are normally incorporated into trial wavefunctions and trial Hamiltonians. Minimization of the ground-state energy with respect to such variational parameters is the famous Rayleigh–Ritz method. Accurate approximations for excited states can also be obtained by means of variational procedures [1–10]. In field theory, one includes variational parameters into a trial Gaussian action [2, 11–14], which is equivalent to the inclusion of such parameters into a trial Hamiltonian in statistical mechanics [15].

Among nonstandard variational procedures, we may mention the method of potential envelopes [16–18] where the minimization of eigenenergies is defined with respect to average kinetic energy. In the variational coherent anomaly method [19], one extremizes the free energy with respect to parameters of a gauge transformation. In the minimum-element approach [20], the perturbation series is varied with respect to the number of perturbation order.

One of the most interesting and difficult cases is that of Hamiltonian with an anharmonic double-well potential. This problem not only serves as a good illustration of difficulties characteristic of approximate calculations for nontrivial potentials, but is of interest itself, since double-well potentials model various phenomena encountered in physics and chemistry. The spectrum of the Hamiltonian with an anharmonic double-well potential

has been considered in several approximations of quasiclassical nature [21–24]. The quasiclassical approximation [24] is the most inaccurate for low lying levels where its error is about 20%. There are more accurate numerical calculations, notable among which are: a variational approach employing the particle-in-box trial functions with two separate bases for even and odd states [24], the finite-difference technique [25], the hypervirial recurrence-relation scheme [26–28], the renormalized hypervirial-Padé scheme [29–31], the variational matrix solution [32], the Rayleigh–Ritz variational method supplemented by the Lanczos algorithm [33], and the Brillouin–Wigner perturbation theory based on shifted oscillator variational functions [34]. The most difficult for the double-well potential is the calculation of the low lying nearly degenerate states for which even quite sophisticated techniques, such as the renormalized hypervirial-Padé scheme [29–31], fail.

Although there exist methods [32–34], involving extensive numerical calculations, which permit one to get accurate eigenvalues for the double-well potential, it would also be important to have explicit analytical expressions for these eigenvalues. Such explicit expressions should be sufficiently simple and accurate providing correct asymptotic expansions for both weak and strong coupling limits. However, in reaching this goal one is confronted with the following obstacles. (i) In the weak coupling limit, the dependence of eigenvalues on the coupling parameter is nonanalytical, that the expansion in powers of this parameter kills the level splitting characteristic of the double-well potential. (ii) Variational equations being, generally, nonlinear often have nonunique solutions for trial parameters. If some of these solutions are close to each other, it is difficult, if at all possible, to distinguish between them. Precisely this case occurs in the strong coupling limit of the double-well potential. (iii) In the intermediate region of the coupling parameter, points may exist at which some eigenvalues cross zero. Such points can be called critical because in their neighbourhood the errors of approximate calculations dramatically increase.

Below, we obtain simple analytical formulae for the spectrum of the Hamiltonian with an anharmonic double-well potential. We give recipes for treating the difficulties outlined above. This permits us to derive accurate asymptotic expansions for the weak coupling as well as strong coupling limits. The main attention we pay to the most difficult case of low lying states, showing that even for them our formulae provide quite accurate results within an error not exceeding 3% in the whole range of the coupling parameter, from zero to infinity. These results, if one wishes to improve accuracy, serve as a starting approximation for an iteration procedure.

2. Double-well potential

We consider a model with the double-well potential described by the Hamiltonian

$$\hat{H} = -\frac{1}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} - \frac{1}{2}m\omega^2 x^2 + \lambda m^2 x^4 \tag{1}$$

in which $x \in \mathbb{R}$, and m, ω and λ are positive constants. By scaling, it is convenient to reduce (1) to the dimensionless form

$$H = -\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}x^2} - \frac{1}{2}x^2 + gx^4 \tag{2}$$

whose eigenvalues are related to those of (1), denoted by $E(\lambda)$, as

$$e(g) = \frac{E(\lambda)}{\omega} \qquad g \equiv \frac{\lambda}{\omega^3}. \tag{3}$$

To return from (2) to (1), one should make the substitution

$$x \to \sqrt{m\omega}x \qquad H \to \hat{H}/\omega.$$

As a trial wavefunction for (2) it is natural to take the linear combination

$$\psi_n^{(0)}(x) = A\varphi_n^+(x) + B\varphi_n^-(x) \tag{4}$$

of the shifted oscillator functions

$$\varphi_n^\pm(x) \equiv \varphi_n(x \pm \sigma)$$

$$\varphi_n(x) = \frac{(u/\pi)^{1/4}}{\sqrt{2^n n!}} \exp\left(-\frac{1}{2}ux^2\right) H_n(\sqrt{u}x) \tag{5}$$

in which $H_n(\cdot)$ is a Hermite polynomial, and $n = 0, 1, 2, \ldots$. Normalizing the functions (4),

$$\|\psi_n\|^2 \equiv (\psi_n, \psi_n) = 1 \tag{6}$$

we have

$$A^2 + 2\eta AB + B^2 = 1 \tag{7}$$

where

$$\eta \equiv (\varphi_n^+, \varphi_n^-) \tag{8}$$

is the overlap integral. Equation (7) can be treated as defining $B = B(A)$.

Thus, there are three variational parameters: u, σ and A, to be found by extremizing the energy

$$E_n(g, u, \sigma, A) = (\psi_n, H\psi_n). \tag{9}$$

From the variational equation

$$\frac{\partial}{\partial A}E_n(g, u, \sigma, A) = 0 \tag{10}$$

we find two parameters

$$A^+ = \frac{1}{\sqrt{2(1+\eta)}} \qquad A^- = \frac{1}{\sqrt{2(1-\eta)}} \tag{11}$$

and, respectively, from (7) we get

$$B(A^+) = A^+ \qquad B(A^-) = -A^-$$

which reflects the existence of two kinds of states, symmetric and antisymmetric. Since the variational equations are written for each level labelled by the index $n = 0, 1, 2, \ldots$, variational parameters, certainly, also depend on the number n. However, for the sake of notation brevity, we do not show this dependence explicitly.

For the energy levels (9) we have

$$E^+(g, u, \sigma) \equiv E_n(g, u, \sigma, A^+) = \frac{p+q}{1+\eta} \tag{12}$$

and

$$E^-(g, u, \sigma) \equiv E_n(g, u, \sigma, A^-) = \frac{p-q}{1-\eta} \tag{13}$$

where the notation

$$p \equiv (\varphi_n^+, H\varphi_n^+) = (\varphi_n^-, H\varphi_n^-)$$
$$q \equiv (\varphi_n^+, H\varphi_n^-) = (\varphi_n^-, H\varphi_n^+) \tag{14}$$

is used. When φ_n^+ does not coincide with φ_n^-, that is if $\sigma \neq 0$, then

$$|\eta| = |(\varphi_n^+, \varphi_n^-)| < \|\varphi_n^+\| \cdot \|\varphi_n^-\| = 1$$

and the denominators in (12) and (13) do not contain zeros. The wavefunction

$$\psi_n^+(x) = A^+[\varphi_n(x + \sigma) + \varphi_n(x - \sigma)] \tag{15}$$

is symmetric for n even and antisymmetric for n odd. Conversely,

$$\psi_n^-(x) = A^-[\varphi_n(x + \sigma) - \varphi_n(x - \sigma)] \tag{16}$$

is antisymmetric for n even and symmetric for n odd. In the case of $n = 0$, the level (12) gives the ground-state energy and (13), the first excited energy level.

With the wavefunctions (5), for the parameters in (14) we obtain

$$p = \tfrac{1}{2}(n + \tfrac{1}{2})u - \tfrac{1}{2}(n + \tfrac{1}{2} + \xi)\frac{1}{u} + \tfrac{1}{2}[3(n^2 + n + \tfrac{1}{2}) + 12(n + \tfrac{1}{2})\xi + 2\xi^2]\frac{g}{u^2}$$

$$q = \tfrac{1}{2}e^{-\xi}\left\{[(2n + \tfrac{3}{2} - \xi)L_n^0(2\xi) - L_n^1(2\xi)]u - \tfrac{1}{2}[2L_n^1(2\xi) - L_n^0(2\xi)]\frac{1}{u}\right. \tag{17}$$

$$\left. + \tfrac{3}{2}[L_n^0(2\xi) - 4L_n^1(2\xi) + 4L_n^2(2\xi)]\frac{g}{u^2}\right\}$$

where

$$L_n^l(\xi) = \frac{1}{n!}e^\xi \xi^{-l}\frac{d^n}{d\xi^n}(e^{-\xi}\xi^{n+l}) = \sum_{m=0}^n \frac{\Gamma(n + l + 1)(-\xi)^m}{\Gamma(m + l + 1)(n - m)!m!}$$

is the associate Laguerre polynomial, and

$$\xi \equiv u\sigma^2. \tag{18}$$

The overlap integral (8) becomes

$$\eta = e^{-\xi}L_n^0(2\xi). \tag{19}$$

For the case $n = 0$, this simplifies to

$$p = \frac{1}{4}\left[u - (1 + 2\xi)\frac{1}{u} + (3 + 12\xi + 4\xi^2)\frac{g}{u^2}\right]$$

$$q = \frac{1}{4}e^{-\xi}\left[(1 - 2\xi)u - \frac{1}{u} + 3\frac{g}{u^2}\right] \tag{20}$$

$$\eta = e^{-\xi} \qquad (n = 0).$$

3. Variational solution

The variational equations for the parameters u and σ are

$$\frac{\partial}{\partial u}E^\pm(g, u, \sigma) = 0 \qquad \frac{\partial}{\partial\sigma}E^\pm(g, u, \sigma) = 0 \tag{21}$$

which define $u^\pm(g)$ and $\sigma^\pm(g)$. Substituting the latter back into (12) and (13), we obtain

$$e^\pm(g) \equiv E^\pm(g, u^\pm(g), \sigma^\pm(g)). \tag{22}$$

The most difficult problem for the double-well potential, as is known, is the calculation of low-lying energy levels. Therefore we shall pay greatest attention in what follows just to these states. The ground state corresponds to $n = 0$ and

$$u = u^+(g) \qquad \sigma = \sigma^+(g)$$
$$\xi = u^+(g)[\sigma^+(g)]^2 = \xi^+(g) \tag{23}$$
$$\eta = \exp\{-\xi^+(g)\} = \eta^+(g).$$

The variational equations in (21) give

$$u^3 + (1 - 2\xi)\eta u^3 + (1 + 2\xi + \eta)u - 2g(3 + 12\xi + 4\xi^2 + 3\eta) = 0$$
$$(1 - \xi + \eta)\eta u^3 + u + (1 + \xi)\eta u - 2g(3 + 2\xi) - 2g\eta(3 + 5\xi + \xi^2) = 0. \tag{24}$$

The solution of (24) defines the ground-state energy

$$e^+(g) = \frac{1}{8u}\left(3u^2 - 1 - 2\xi\frac{1 + 3\eta u^2}{1 + \eta}\right). \tag{25}$$

The first excited state corresponds to $n = 0$ and

$$u = u^-(g) \qquad \sigma = \sigma^-(g)$$
$$\xi = u^-(g)[\sigma^-(g)]^2 = \xi^-(g) \tag{26}$$
$$\eta = \exp\{-\xi^-(g)\} = \eta^-(g).$$

The variational equations for this case, following from (21), are almost the same as (24), and differ from (24) only by the change $\eta \to -\eta$. The energy of the first excited level is

$$e^-(g) = \frac{1}{8u}\left(3u^2 - 1 - 2\xi\frac{1 - 3\eta u^2}{1 - \eta}\right). \tag{27}$$

An important quantity is the gap

$$\Delta(g) \equiv e^-(g) - e^+(g) \tag{28}$$

between the energy levels (27) and (25). This gap is proportional to the exponential of the instanton action [22]. Calculating (28) we should not forget that u, ξ and η are different for (25) and (27), being defined as (23) and (26), respectively.

To find (25) and (27), we need to solve the variational equations, that is (24) and the related equations in which η is replaced by $(-\eta)$. These equations, for any value of the coupling parameter g, always have two solutions for each of the quantities, u^+ and σ^+ as well as for u^- and σ^-. One solution contains $\sigma^\pm = 0$; another $\sigma^\pm \neq 0$. The first of these solutions, as is clear, corresponds to a single-well potential, while the second corresponds to a double-well potential. Therefore, we need to separate out the second solution with $\sigma^\pm \neq 0$. This is straightforward in the weak coupling limit, when $\sigma^\pm \to \infty$, but not in the strong coupling limit, when $\sigma^\pm \to 0$.

Wishing to derive an asymptotic expansion for the weak coupling limit, one encounters another problem. An expansion in powers of g kills the level splitting making $e^+(g)$ and $e^-(g)$ coincide. To overcome this deficiency, we invoke the so-called *composite asymptotic expansion*: first, we look for an expansion with respect to two parameters, g and η, and then consider $\eta = \eta(g)$ as a function of g. This gives us

$$u^\pm(g) \simeq u_0(g) \mp a(g)\eta(g)$$
$$\xi^\pm(g) \simeq \xi_0(g) \mp b(g)\eta(g) \tag{29}$$
$$\sigma^\pm(g) \simeq \sigma_0(g) \mp c(g)\eta(g)$$

where $g \to 0$ and the overlap integral is

$$\eta(g) = \exp\left(-\frac{1}{2\sqrt{2}}g^{-1} + \frac{9}{4} + \frac{27}{8\sqrt{2}}g\right). \tag{30}$$

Other functions in (29) are

$$u_0(g) = \sqrt{2} - 3g - \frac{27}{2\sqrt{2}}g^2$$

$$\xi_0(g) = \frac{1}{2\sqrt{2}}g^{-1} - \frac{9}{4} - \frac{27}{8\sqrt{2}}g$$

$$\sigma_0(g) = \frac{1}{2}g^{-1/2} - \frac{3}{2\sqrt{2}}g^{1/2}$$

$$a(g) = \frac{3}{16\sqrt{2}}g^{-2} - \frac{17}{8}g^{-1} + \frac{561}{64\sqrt{2}} + \frac{27}{2}g \tag{31}$$

$$b(g) = \frac{3}{64\sqrt{2}}g^{-3} - \frac{11}{32}g^{-2} - \frac{559}{256\sqrt{2}}g^{-1} + \frac{207}{16} + \frac{78\,057}{2048\sqrt{2}}g$$

$$c(g) = \frac{21}{64\sqrt{2}}g^{-3/2} + \frac{125\,289}{4096}g^{-1/2} + \frac{425\,811}{2048\sqrt{2}}g^{1/2}.$$

Substituting (29)–(31) into (25) and (27), we obtain

$$e^{\pm}(g) \simeq e_0(g) \mp \tfrac{1}{2}\Delta(g) \tag{32}$$

where

$$e_0(g) = -\frac{1}{16}g^{-1} + \frac{1}{\sqrt{2}} - \frac{21}{64}g \tag{33}$$

and the gap (28) is

$$\Delta(g) = \left(\frac{303}{1024}g^{-1} - \frac{981}{512\sqrt{2}} + \frac{10\,773}{8192}g\right)\eta(g). \tag{34}$$

Leaving in (34) and (30) only the main terms, we see that the splitting gap

$$\Delta(g) \simeq \frac{303}{1024}g^{-1}\exp\left(-\frac{1}{2\sqrt{2}}g^{-1}\right) \tag{35}$$

becomes exponentially small at $g \ll 1$ and disappears as $g \to 0$. This effect is called quasidegeneracy. The composite asymptotic expansion permits us to describe the splitting of the levels in (32).

4. Restricted variation

As discussed above, the variational equation (24) has nonunique solutions, one corresponding to a single-well potential and another related to the double-well potential. These solutions become close to each other at $g \gg 1$ making it difficult to write a correct asymptotic expansion for the strong coupling limit as $g \to \infty$. To eliminate this nonuniqueness separating out the correct solution, the *restricted variational procedure* can be employed. To this end, we notice that the potential of the Hamiltonian (2), that is

$$V(x) = -\tfrac{1}{2}x^2 + gx^4 \tag{36}$$

has the minimum

$$\min_{x \in \mathbb{R}} V(x) = V(x^{\pm}) = -\frac{1}{16g} \tag{37}$$

at the coordinates

$$x^{\pm} = \pm \frac{1}{2\sqrt{g}} \equiv x^{\pm}(g). \tag{38}$$

In order to rule out the solution with the zero $\sigma^{\pm}$, let us impose the constraint

$$\sigma^{\pm} \equiv x^{\pm}(g) = \pm \frac{1}{2\sqrt{g}} \tag{39}$$

restricting the shifts of the position of the minimum (37) by the nonzero values in (38).

Considering the functions

$$\xi^{\pm}(g) = \frac{u^{\pm}(g)}{4g} \qquad \eta^{\pm}(g) = \exp\{-\xi^{\pm}(g)\} \tag{40}$$

under the constraint (39), in place of (20), we have

$$p = \frac{1}{4}\left(u - \frac{1}{4g} + \frac{2}{u} + \frac{3g}{u^2}\right)$$
$$q = \frac{1}{4}\left(u - \frac{u^2}{2g} - \frac{1}{u} + \frac{3g}{u^2}\right)\exp\left(-\frac{u}{4g}\right). \tag{41}$$

Now, instead of two equations in (21), we have one variational equation

$$\frac{\partial}{\partial u}E^{\pm}(g, u, x^{\pm}) = 0. \tag{42}$$

For the ground-state level E^+ this yields

$$64\eta g^2\xi^5 - 128\eta(1+\eta)g^2\xi^4 + 32(1+\eta)^2g^2\xi^3 - 2\eta\xi^3 + 6\eta\xi^2$$
$$-2(1+\eta)(2-\eta)\xi - 3(1+\eta)^2 = 0. \tag{43}$$

For the first excited level E^-, the variational equation is similar to (43) with the change $\eta \to -\eta$. Equation (43), in contrast to (24), does not contain the zero solution for ξ. In the weak coupling limit, the restricted variational approach gives the following composite asymptotic expansions:

$$u^{\pm} \simeq u_0(g) \mp a(g)\eta(g)$$
$$\xi^{\pm}(g) \simeq \xi_0(g) \mp b(g)\eta(g) \tag{44}$$

where $g \to 0$ and the overlap integral is

$$\eta(g) = \exp\left(-\frac{1}{2\sqrt{2}}g^{-1} - \frac{3}{8} + \frac{27}{32\sqrt{2}}g - \frac{27}{16}g^2\right) \tag{45}$$

other functions being

$$u_0(g) = \sqrt{2} + \frac{3}{2}g - \frac{27}{8\sqrt{2}}g^2$$
$$\xi_0(g) = \frac{1}{2\sqrt{2}}g^{-1} + \frac{3}{8} - \frac{27}{32\sqrt{2}}g + \frac{27}{16}g^2$$
$$a(g) = \frac{3}{16\sqrt{2}}g^{-2} - \frac{1}{4}g^{-1} - \frac{207}{256\sqrt{2}} - \frac{9}{64}g + \frac{101385}{8192\sqrt{2}}g^2 \tag{46}$$
$$b(g) = \frac{3}{64\sqrt{2}}g^{-3} - \frac{1}{16}g^{-2} - \frac{207}{1024}g^{-1} - \frac{9}{256} + \frac{101\,385}{32\,768\sqrt{2}}g - \frac{1\,683\,261}{131\,072}g^2.$$

The eigenvalues in this limit have the same form as in (32) with

$$e_0(g) = -\frac{1}{16}g^{-1} + \frac{1}{\sqrt{2}} + \frac{3}{8}g \tag{47}$$

and the splitting gap

$$\Delta(g) = \left(\frac{3}{8}g^{-1} + \frac{3}{\sqrt{2}} - \frac{9}{4}g\right)\eta(g). \tag{48}$$

Comparing our analytical results with numerical calculations [32–34], we find that, in the weak coupling limit, the accuracy of the restricted variational procedure is slightly worse than the accuracy of the procedure in section 3. However, the advantage of the restricted variational procedure comes into play in the strong coupling limit, where it has the same accuracy as the procedure of section 3 but, in contrast to the latter, allows a straightforward asymptotic expansion. Thus, in the strong coupling limit we get

$$u^+(g) \simeq (6g)^{1/3} - \tfrac{1}{3}(6g)^{-1/3} + \tfrac{5}{16}(6g)^{-1} - \tfrac{119}{1296}(6g)^{-5/3} + \tfrac{4171}{62\,208}(6g)^{-7/3}$$

$$u^-(g) \simeq (10g)^{1/3} - \tfrac{8}{9}(10g)^{-1/3} + \tfrac{65}{48}(10g)^{-1} - \tfrac{4241}{4374}(10g)^{-5/3} + \tfrac{4\,897\,291}{5\,038\,848}(10g)^{-7/3}.$$

This leads to the eigenvalues

$$e^+(g) \simeq \tfrac{3}{8}(6g)^{1/3} - \tfrac{1}{4}(6g)^{-1/3} + \tfrac{17}{24}(6g)^{-1}$$
$$e^-(g) \simeq \tfrac{9}{8}(10g)^{1/3} - \tfrac{3}{4}(10g)^{-1/3} + \tfrac{287}{144}(10g)^{-1} \tag{49}$$

for $g \to \infty$, with the gap (28) becoming

$$\Delta(g) \simeq 1.742\,319g^{1/3} - 0.210\,539g^{-1/3} + 0.081\,250g^{-1}. \tag{50}$$

The leading terms of $e^+(g)$ and $e^-(g)$ correspond to the ground state and first excited level of the single-well anharmonic oscillator [6, 7], respectively. But the following terms are, of course, different; the energy levels of the double-well oscillator are lower than the corresponding levels of the single-well oscillator.

5. Positive shift

Let us compare in detail the results of our variational calculations with the numerical data [32–34] that can be considered as exact. Denoting the latter through $E^\pm(g)$, we characterize the accuracy of the approximate values $e^\pm(g)$ by the percentage error.

$$\varepsilon^\pm(g) \equiv \frac{e^\pm(g) - E^\pm(g)}{|E^\pm(g)|} \times 100\%. \tag{51}$$

When either the level number $n \gg 1$ or the coupling parameter $g \gg 1$, we are very close to the case of the single-well anharmonic oscillator [6, 7]; the error (51) being about the same as that of the latter, that is not exceeding 2%. The worst accuracy for the double-well potential is when $n = 0$ and $g < 0.5$. Therefore we must pay greatest attention just to this region. The accuracy of the eigenvalues (25) and (27) for $g < 1.5$ is illustrated by table 1. One can immediately notice that there is a dangerous region of the coupling parameters inside the interval $0.03 < g < 0.3$, where the error (51) strongly increases. Does this signify a drawback of the calculational procedure?

We can sharpen the question even more by noticing that, varying g, we can always find such critical values of g for which

$$E^\pm(g) = 0 \qquad g = g_c^\pm. \tag{52}$$

Table 1. The accuracy of the variational eigenvalues $e^{\pm}(g)$ for the double-well oscillator in the most dangerous region of g where the errors $\varepsilon^{\pm}(g)$ are maximal.

g	$E^+(g)$	$\varepsilon^+(g)$ (%)	$E^-(g)$	$\varepsilon^-(g)$ (%)
0.000 500	−124.29	0.0014	−124.29	0.0014
0.001 414	−43.488	0.0008	−43.488	0.0008
0.003 043	−19.836	0.0039	−19.836	0.0039
0.008 607	−6.5635	0.034	−6.5635	0.034
0.015 811	−3.2625	0.14	−3.2625	0.14
0.026 997	−1.6387	0.55	−1.6371	0.47
0.044 721	−0.762 52	2.8	−0.726 88	1.0
0.062 500	−0.427 60	3.5	−0.311 97	1.8
0.176 780	0.04872	5.0	0.605 64	0.39
0.500 000	0.328 82	0.37	1.4172	0.12
1.414 200	0.615 20	0.17	2.3574	0.076

At such critical points $g_c^{\pm}$, where the eigenvalues cross zero, the error (51) diverges: $\varepsilon^{\pm}(g) \to \infty$. Does it mean the failure of the procedure?

No. This only means that the problem is incorrectly posed and should be modified so as to avoid the appearance of zeros in the denominator of (51). The latter can be done by shifting the Hamiltonian (2) with a nonoperator term $\pi(g)$ getting

$$H_{\pi} \equiv H + \pi(g) \qquad \pi(g) \geqslant \left| \min_{x \in \mathbb{R}} V(x) \right| \tag{53}$$

where the potential $V(x)$ is defined in (36). Because of the nonoperator character of the shift $\pi(g)$, the problem is mathematically the same. But as far as the shifted potential $V(x) + \pi(g) > 0$ is non-negative, the shifted eigenvalues of (2) are positive:

$$E_{\pi}^{\pm}(g) \equiv E^{\pm}(g) + \pi(g) > 0. \tag{54}$$

The accuracy of the shifted approximate eigenvalues

$$e_{\pi}^{\pm}(g) \equiv e^{\pm}(g) + \pi(g) \tag{55}$$

is characterized by the error

$$\varepsilon_{\pi}^{\pm}(g) \equiv \frac{e_{\pi}^{\pm}(g) - E_{\pi}^{\pm}(g)}{|E_{\pi}^{\pm}(g)|} \times 100\%. \tag{56}$$

The latter, owing to (54), never contains zeros in the denominator. The errors (51) and (56) are connected through the relation

$$\varepsilon_{\pi}^{\pm}(g) = \varepsilon^{\pm}(g) \left| \frac{E^{\pm}(g)}{E_{\pi}^{\pm}(g)} \right|.$$

Thus, shifting a Hamiltonian in order to make its spectrum positive definite one gets *positive definite shift*. This way of shifting the sought quantities can be used not only for calculating the spectra of Hamiltonians but for any other cases in which one encounters similar incorrectness in defining the errors.

It is reasonable to choose the shift $\pi(g)$ as

$$\pi(g) \equiv \left| \min_{x \in \mathbb{R}} V(x) \right| = \frac{1}{16g}. \tag{57}$$

Then we may easily redefine all formulae for the eigenvalues obtained in the previous sections. For example, in the weak coupling limit, for the shifted eigenvalues we have

$$e_{\pi}^{\pm}(g) \simeq e_{\pi}^0(g) \mp \tfrac{1}{2}\Delta(g) \qquad (g \to 0) \tag{58}$$

with

$$e_\pi^0(g) = \frac{1}{\sqrt{2}} - \frac{21}{64}g \tag{59}$$

and the same splitting gap as in (34). And in the strong coupling limit we obtain

$$\begin{aligned}
e_\pi^+(g) &\simeq \tfrac{3}{8}(6g)^{1/3} - \tfrac{1}{4}(6g)^{-1/3} + \tfrac{13}{12}(6g)^{-1} \\
e_\pi^-(g) &\simeq \tfrac{9}{8}(10g)^{1/3} - \tfrac{3}{4}(10g)^{-1/3} + \tfrac{377}{144}(10g)^{-1}
\end{aligned} \tag{60}$$

where $g \to \infty$; the gap $\Delta(g)$ being the same as in (50). The accuracy of the shifted eigenvalues (55), in the most dangerous region of g where the errors are maximal, is illustrated in table 2. Now the maximal error is about 3%.

Table 2. The accuracy of the shifted eigenvalues $e_\pi^\pm(g)$ in the dangerous region of g, as compared to the shifted numerical values $E_\pi^\pm(g)$.

g	$E_\pi^+(g)$	$\varepsilon_\pi^+(g)$ (%)	$E_\pi^-(g)$	$\varepsilon_\pi^-(g)$ (%)
0.000 500	0.710 00	0.25	0.710 00	0.25
0.001 414	0.712 85	0.049	0.712 85	0.049
0.003 043	0.702 94	0.11	0.702 94	0.11
0.008 607	0.698 03	0.32	0.698 03	0.32
0.015 811	0.690 44	0.66	0.690 44	0.66
0.026 997	0.676 37	1.3	0.677 97	1.1
0.044 721	0.635 03	3.3	0.670 67	1.1
0.062 500	0.572 40	2.6	0.688 03	0.82
0.176 780	0.402 27	0.61	0.959 19	0.25
0.500 000	0.453 82	0.27	1.5422	0.11
1.414 200	0.659 39	0.16	2.4016	0.075

6. Higher approximations

Our main goal here has been to show the ways of obtaining analytical formulae which would be simple and at the same time sufficiently accurate. The accuracy achieved, within the error of 3%, seems to be quite reasonable for such simple calculations. This accuracy is practically the same as for the single-well anharmonic oscillator [6, 7] for which the renormalized first-order perturbation theory gives the maximal error of 2%.

Singe-shot approximations have always been very important in quantum mechanics allowing us to grasp the principal features of the problem under consideration. This is especially true when such a first approximation successively combines relative simplicity with reasonable accuracy.

However, some dissatisfaction remains when there is no indication of a possible way for a systematic improvement of the results so that an arbitrary accuracy could be achieved if desired. To get rid of this dissatisfaction, we need to delineate a scheme permitting us to obtain successive approximations. In our case, we cannot simply resort to the standard Rayleigh-Schrödinger perturbation theory since we started with a trial wavefunction but the corresponding approximate Hamiltonian was not defined. Another, although not as serious hindrance, is that the basis of trial wavefunctions in (4) is not orthogonal. Nevertheless, a consistent scheme can be constructed with the help of some iteration procedure [34, 35]—this idea is clearly based on the Brillouin–Wigner perturbation theory.

Consider the eigenproblem

$$H\psi_n = E_n\psi_n \qquad (\psi_m, \psi_n) = \delta_{mn} \tag{61}$$

whose rigorous solution cannot be found analytically. Let us start, as we did above, with a basis $\{\psi_n^{(0)}\}$ of trial wavefunctions. These functions can always be normalized but they are not necessarily orthogonal, that is, in the scalar product

$$\alpha_{mn} \equiv (\psi_m^{(0)}, \psi_n^{(0)}) \qquad \alpha_{nn} = 1 \tag{62}$$

the nondiagonal elements α_{mn} are not, generally, zero.

Expand the solution of (61) in the basis $\{\psi_n^{(0)}\}$, so that

$$\psi_n = \sum_j c_{nj}\psi_j^{(0)} \qquad c_{nn} = 1 \tag{63}$$

where the equality $c_{nn} = 1$ is a necessary condition for the validity of (63) in the case when $\psi_n^{(0)} \to \psi_n$. Substituting (63) into (61) and taking a scalar product with $\psi_m^{(0)}$, we get

$$\sum_j c_{nj}(H_{mj} - E_n\alpha_{mj}) = 0 \tag{64}$$

where we use the notation

$$H_{mn} \equiv (\psi_m^{(0)}, H\psi_n^{(0)}). \tag{65}$$

Separating in (64) the term with $j = n$ from those with $j \neq n$, we have

$$c_{mn} = -\sum_{j(\neq n)} c_{mj} \frac{E_m\alpha_{nj} - H_{nj}}{E_m - H_{nn}} \tag{66}$$

and on the other hand (64) yields

$$E_n = \frac{\sum_j c_{nj}H_{nj}}{\sum_j c_{nj}\alpha_{nj}}. \tag{67}$$

Equations (66) and (67) are the equations defining c_{mn} and E_n. We stress that until now no approximation has been used. So, (66) and (67) are exact relations.

The solution of (66) and (67) can be realized through the iteration procedure given by the scheme

$$E_n^{(k+1)} = \frac{\sum_j c_{nj}^{(k)} H_{nj}}{\sum_j c_{nj}^{(k)}\alpha_{nj}} \tag{68}$$

where the upper index stands for an iteration step and the coefficients are

$$c_{mn}^{(k+1)} = -\sum_{j(\neq n)} c_{mj}^{(k)} \frac{E_m^{(k+1)}\alpha_{nj} - H_{nj}}{E_m^{(k+1)} - H_{nn}}. \tag{69}$$

Note that for realizing this iteration procedure we do not need to have some initial approximate Hamiltonian. All we need is to choose a basis $\{\psi_n^{(0)}\}$, not necessarily orthogonal, and then, after calculating the matrix element (65), we directly follow the iteration scheme (68) and (69). Thus, starting from $c_{nj}^{(0)} = \delta_{nj}$, we get the natural first approximation for the spectrum

$$E_n^{(1)} = H_{nn} \tag{70}$$

following from (68). Then, from (69) we find

$$c_{mn}^{(1)} = -\frac{E_m^{(1)}\alpha_{nm} - H_{nm}}{E_m^{(1)} - H_{nn}}.$$

The found $c_{mn}^{(1)}$ is to be substituted into (68), which gives $E_n^{(2)}$, and so on. In this way, we can proceed until any approximation order desired. The variational parameters entering into the trial wavefunction are to be defined at each step of the procedure. In the case of several choices, the optimal parameters are those that provide the better stability of numerical calculations [36, 37].

For the double-well oscillator, the basis $\{\psi_n^{(0)}\}$ is made of the trial wavefunctions in (4). The iteration procedure converged sufficiently fast, so that a few first iterations yield the eigenvalues $E^\pm(g)$ from table 1, or respectively, $E_\pi^\pm(g)$ from the table 2, which have been treated as exact numerical results [32–34]. The number of iteration steps depends on the value of the coupling parameter g, but the procedure always converges to the exact energy levels given in the tables. The convergence of the procedure can be accelerated by invoking the renormalization-group tricks [38, 39]. But too extensive numerical computation is not the aim of the present paper.

7. Discussion

Let us emphasize once again that our main aim here has been to present analytical formulae that would be relatively simple and at the same time sufficiently accurate in the whole range of coupling parameters, from zero to infinity. The accuracy of the first approximation, being 3%, seems to be quite satisfactory. Futher approximations can be obtained numerically by following the iteration procedure described in the previous section, so that an arbitrary accuracy can be achieved if desired.

Considering analytical expressions we paid attention to technical difficulties that are typical of such calculations and are often met in the eigenproblems dealing with nonmonotonous potentials. We suggested the remedies for treating these difficulties. Some recipes, after being formulated, may look quite simple because they are natural. This concerns the positive definite shift of section 5. However, as is known, solutions almost always look simpler afterwards, although they are not evident *a priori*. The fact that the ill-posed problems, which can be treated by the positive shift, repeatedly appear in literature unambiguously proves that this question has had to be formulated explicitly.

The restricted variation of section 4 suggests a simple way of obtaining asymptotic expansions in the strong coupling limit. Recall again that we are mainly concerned about analytical calculations in the course of which the suggested method of freezing one or some of the variational parameters seems to be the simplest for solving the problem of multiple solutions. And when we are entangled into heavy numerical computations of higher approximations, other selection methods [36,37] may be more appropriate.

Recall also that we are using the restricted variation for getting explicit expressions in the strong coupling limit, when $g \to \infty$. In this limit, the freezing of the variational parameter σ does not worsen the approximation since in the restricted as well as in he unrestricted variations $\sigma \to 0$ as $g \to \infty$, as a result of which both procedures quickly converge to one another. It goes without saying that in the intermediate region of g, and especially in the weak coupling limit, when $g \to 0$, the extremal value of σ is an important variational parameter improving the approximation. Then, of course, one should not freeze σ and we also do not do it.

The variational procedure involving wavefunctions, as described in this paper, is analogous to the procedure involving path integrals, as expounded in the recent monograph [40]. The accuracy of the first three approximations for the double-well potential is also practically the same in both methods. Let us consider, for example, such a delicate

characteristic as the weak-coupling spectrum slope of lower levels comparing it with that

$$\lim_{g \to 0} \frac{\mathrm{d}}{\mathrm{d}g} E_\pi^\pm(g) = -\frac{1}{4}$$

following from an exact asymptotic expansion as $g \to 0$. Our first approximation yields for the slope the value $-\frac{21}{64}$ and the first approximation of Kleinert [40] gives $-\frac{3}{16}$, which differ from the exact slope $-\frac{1}{4}$. However, in both cases the higher approximations correct this deficiency.

It is worth noting that, in any method, the whole spectrum of excited states cannot be obtained without trial wavefunctions. This concerns, of course, the method of path integrals too [40], in which excitation energies can be obtained through the projection of transition amplitudes onto the excited states. To realize this projection, one has to invoke a basis of trial wavefunctions.

Finally, one may ask the question as to whether a method based on trial wavefunctions, but not involving an approximate Hamiltonian, is generalizable to be used in quantum field theory and quantum statistical mechanics. In these theories, the basic quantity is the so-called generating functional which in field theory is also named an effective potential; and in statistical mechanics, a thermodynamical potential,

$$F = -T \ln \operatorname{Tr} e^{-\beta H}$$

where T is temperature and $\beta T \equiv 1$. We possess a large arsenal of approximation methods for calculating F, when we have in hand an approximate Hamiltonian H_0 (or an approximate Lagrangian). Then approximate expressions of F are obtained by means of an expansion in powers of $H - H_0$. But how could we proceed if H_0 is not given? In such a case, we can resort to the energy representation

$$F = -T \ln \sum_n \exp(-\beta E_n).$$

If approximate energy levels $E_n^{(k)}$ are calculated, then the k-approximation of F may be defined as

$$F^{(k)} \equiv -T \ln \sum_n \exp(-\beta E_n^{(k)}).$$

Thus, we obtain the sequence $\{F^{(k)} | k = 0, 1, 2, \ldots\}$ of approximate effective potentials.

Acknowledgment

References

[1] Killingbeck J 1981 *J. Phys. A: Math. Gen.* **14** 1005
[2] Stevenson P M 1981 *Phys. Rev.* D. **23** 2916
[3] Feranchuk I D and Komarov L I 1982 *Phys. Lett.* **88A** 211
[4] Lai C S and Madan M P 1985 *Mol. Phys.* **54** 669
[5] Fernández F M, Mesón A M and Castro E A 1986 *Mol. Phys.* **58** 365
[6] Yukalova E P and Yukalov V I 1993 *J. Phys. A: Math. Gen.* **26** 2011
[7] Yukalova E P and Yukalov V I 1993 *Phys. Lett.* **175A** 27
[8] Chandra A and Bhattacharyya K 1994 *Pramana J. Phys.* **43** 117
[9] Pathak R and Bhattacharyya K 1994 *Chem. Phys. Lett.* **230** 437
[10] Dineykhan M and Efimov G 1995 *Yad. Fiz.* **58** 1614
[11] Okopinska A 1993 *Ann. Phys.* **228** 19

[12] Kleinert H. 1993 *Phys. Lett.* **300B** 261
[13] Sisakyan A N and Solovtsov I L 1994 *Phys. Part. Nucl.* **25** 478
[14] Solovtsov I L and Solovtsova O P 1995 *Phys. Lett.* **344B** 377
[15] Yukalov V I and Yukalova E P 1994 *Physica* **206A** 553
[16] Hall R 1992 *J. Math. Phys.* **33** 1710
[17] Hall R 1992 *J. Phys. A: Math. Gen.* **25** 1373
[18] Hall R 1995 *J. Phys. A: Math. Gen.* **28** 1771
[19] Kolesik M and Šamaj L 1993 *J. Stat. Phys.* **72** 1203
[20] Lee T 1995 *Nucl. Phys.* B **436** 129
[21] Yuste S B and Sánchez A M 1993 *Phys. Rev.* A **48** 3478
[22] Dobrokhotov S Y and Kolokoltsov V N 1993 *Teor. Mat. Fiz.* **94** 426
[23] Kleinert H 1994 *Phys. Lett.* **190A** 131
[24] Pathak R and Bhattacharyya K 1995 *Int. J. Quantum Chem.* **54** 13
[25] Witwit M R M 1992 *J. Phys. A: Math. Gen.* **25** 503
[26] Hodgson R J and Varshni Y P 1989 *J. Phys. A: Math. Gen.* **22** 61
[27] Handy C R 1992 *Phys. Rev.* A **46** 1663
[28] Witwit M R and Killingbeck J P 1993 *Can. J. Phys.* **71** 475
[29] Bansal M, Srivastava S and Vishwamittar 1991 *Phys. Lett.* **44A** 8012
[30] Srivastava S and Vishwamittar 1991 *Mol. Phys.* **72** 1285
[31] Mamta and Vishwamittar 1995 *Physica* **216A** 452
[32] Balsa R, Plo M, Esteve J and Pacheco A 1983 *Phys. Rev.* D **28** 1945
[33] Bishop R, Flynn M, Bosca M and Guardiola R 1989 *Phys. Rev.* A **40** 6154
[34] Arias de Saavedra F and Buendia E 1990 *Phys. Rev.* A **42** 5073
[35] Yukalova E P and Yukalov V I 1992 *Bulg. J. Phys.* **19** 12
[36] Janke W and Kleinert H 1995 *Phys. Rev. Lett.* **75** 2787
[37] Kleinert H and Janke W 1995 *Phys. Lett.* **206A** 283
[38] Yukalov V I 1991 *J. Math. Phys.* **32** 1235
[39] Yukalov V I 1992 *J. Math. Phys.* **33** 3994
[40] Kleinert H 1995 *Path Integrals in Quantum Mechanics, Statistics and Polymer Physics* (Singapore: World Scientific)