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Accuracy of semiclassics: Comparative analysis of WKB and instanton approaches

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Abstract

We analyze quantitatively the accuracy of eigenfunction and eigenvalue calculations in the frame work of WKB and instanton semiclassical methods. We show that to estimate the accuracy it is enough to compare two linearly independent (with the same quantum number) solutions to the Schrödinger equations with the potential under study, and with the approximating piecewise smooth potential. The main advantage of the approach is related to the appropriate choice of the approximating potential, providing absolutely convergent majorant series for the solutions. We test our method for a strongly anharmonic one dimensional potential, but the basic ideas inspiring our work and its results can be applied to a large variety of interesting chemical and physical problems which are of relevance to various molecular systems.

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1 Introduction

It is a textbook wisdom that if the de Broglie wavelengths λ of particles are small in comparison with the characteristic space scales of a given problem, then the problem can be treated semiclassically. The commonly used WKB method (phase integral approach) [1–3] is intended for the conditions of "geometrical optics", in which the gradient of the action σ is large, but slowly variable (this is suggested also by it containing the factor $\hbar$, since we are dealing with a semiclassical approximation, in which $\hbar$ is taken as small). The corresponding condition can be formulated more quantitatively [1] as follows: λ must vary only slightly over distances of the order of itself

$$\left| \frac{d(\lambda(x)/2\pi)}{dx} \right| \ll 1 \,, \tag{1}$$

where $\lambda(x) = 2\pi\hbar/p(x)$, and $p(x)$ is a classical momentum. However, this simple criterion is not a practical tool to estimate how accurate could be found semiclassical solutions of particular problems, since nothing is specified regarding the convergence of the semiclassical series. The criterion (1) does not work to estimate the magnitude of the error involved in the approximate calculation of physical quantities (e.g., matrix elements), neither to find the domain of validity in the complex plane in which the semiclassical solutions are defined. Indeed from (1) one can conclude only that higher order corrections to semiclassical wave functions are small in the asymptotic regions, but this mathematical criterion has almost nothing to do with say the physical accuracy of semiclassical matrix elements which depends on the wave function accuracy in space regions providing main contributions into the matrix elements under consideration. For example, the energy eigenvalues are determined by the asymptotical region of the linear turning points (i.e., the region distant from these points), and as well by the proximity region to the second order turning points, since in the both regions the wave functions possess the largest values.

Within the WKB method such kind of a physical accuracy estimation has been performed long ago by N. and P.O. Fröman [4]. They analyzed higher order corrections to the semiclassical wave functions and found that although those are really small over $1/\gamma^2$ ($\gamma \gg 1$ is semiclassical parameter), the corrections are proportional to the factor $[(E/\gamma) - U]^{-2}$, (where E is energy and U is potential), and thus the function has non-integrable singularity at the linear turning points where $[(E/\gamma) - U] = 0$ (or, within the alternative to WKB semiclassical formalism so-called extreme tunneling trajectory or instanton approach [5–13] the corrections are singular in

the second order turning points). To surmount this problem in [4] (see also [14], and [15]) the analytical continuation of the correction function into the complex plane has been proposed, and it gives impractically bulky expressions even for simple model potentials. Since this problem has relevance far beyond WKB treatment of a particular model potential, this is an issue of general interest to develop a simple and convenient in practice quantitative method to study the accuracy of the semiclassical approach, and it is the immediate motivation of the present paper to develop a systematic procedure how to do it.

The idea of our approach is to construct two linearly independent continuous (with continuous first derivatives) approximate solutions to the Schrödinger equation, which in the asymptotic region coincide with semiclassic solutions, and in the vicinity of the turning points - with the exact solutions of the so-called comparison equation (i.e. the exact solution of the Schrödinger equation for the chosen appropriately approximate near the turning points potentials $V_c(X)$, henceforth will be referred to as the comparison potential). Although, scanning the literature we found one rather old paper [16] with a similar comparison equation approach, but our accuracy criterion is formulated as the majorant inequalities for a certain matrix (which we find in the explicit analytical form and calculated numerically) connecting our approximate and exact solutions in the finite space interval (not only in the vicinity of the turning points). Since this method has largely gone unnoticed in the study of semiclassics, we found it worthwhile to present its derivation in a short and explicit form, and also to point out its practical usability.

The remainder of this paper is organized as follows. In Sect. 2 we present the basic expressions necessary for our investigation. In this section we also present the main steps and qualitative idea of our method. Sect. 3 contains our results. We derive the inequalities which enable us to find the finite space interval (not at the isolated points) where the solutions have to be matched, and calculate the 2×2 coordinate dependent matrix connecting the approximate and exact solutions. Since the semiclassical solutions of the harmonic potential coincide with the exact solutions, the accuracy of any semiclassically treated problem depends crucially on its potential energy anharmonicity. That is why as the touchstone to test our method the results presented in the Sect. 3 are applied to an anharmonic oscillator in Sect. 4. We end with some brief conclusions in the same section.

2 Semiclassical equations in the WKB and instanton forms

Technically the basic idea how to overcome the difficulty of the semiclassical solutions in the vicinity of the turning points is reduced to an appropriate (admitting exact analytic solutions) approximation of the potential near the turning points. After that step one has to match the asymptotics of this exact solution to the Schrödinger equation for an approximate potential with the semiclassical solutions to the Schrödinger equation for the potential under consideration (i.e. approximate solutions of the exact potential) far from the turning points. To illustrate main ideas of any semiclassic method (and to retain compactness and transparency of expressions) we discuss here a one dimensional case. As it is well known [1] in the WKB method solutions to the Schrödinger equation are sought in the form

$$\psi = A \exp\left(\frac{i\sigma}{\hbar}\right), \tag{2}$$

where for the function σ called action the one particle Schrödinger equation (traditionally termed as Hamilton - Jacoby equation) reads as

$$\frac{1}{2m}\left(\frac{\partial\sigma}{\partial x}\right)^2 = E - U\,, \tag{3}$$

where m is a particle mass, E is its energy, and U is external field potential. Since the system is supposed quasi-classical in its properties, we seek σ in the form of a series expanded in powers of $\hbar$. Depending on normalization prefactor $A(x)$ entering (2) can be also found but the corresponding equation (referred traditionally as transport equation) plays a pure passive role since it is fully determined by the action σ found as the solution of the Hamilton - Jacoby equation

$$-\frac{i\hbar}{m}\left[\frac{1}{2}\frac{\partial^2\sigma}{\partial x^2}A + \frac{\partial A}{\partial x}\frac{\partial\sigma}{\partial x}\right] + \frac{\hbar^2}{2m}\frac{\partial^2 A}{\partial x^2} = 0\,, \tag{4}$$

where in the spirit of the semiclassical approximation the last term ($\propto \hbar^2$) is neglected. Technically of course more convenient to use instead of $\hbar$ an expansion over equivalent but dimensionless parameter $\gamma^{-1} \ll 1$ we will call in what follows as semiclassical parameter and define as

$$\gamma \equiv \frac{m\Omega_0 a_0^2}{\hbar} \gg 1\,, \tag{5}$$

where a_0 is a characteristic length of the problem, e.g. the tunneling distance, Ω_0 is a characteristic frequency, e.g. the oscillation frequency around the potential minimum. Evidently the semiclassical parameter $\gamma \gg 1$, and by its physical meaning it is determined by the ratio of the characteristic potential scale over the zero oscillation energy. We put $\hbar = 1$, and use Ω_0 and a_0 to set corresponding dimensionless scales, i.e. we introduce dimensionless energy $\epsilon \equiv E/\gamma\Omega_0$, dimensionless coordinate $X \equiv x/a_0$, dimensionless potential $V \equiv U/\Omega_0$ (except where explicitely stated to the contrary and dimensions are necessary for understanding or numerical estimations).

The analogous to (2), (3) procedure for the Schrödinger equation in the imaginary time (instanton formalism, corresponding to the Wick rotation in the phase space, when coordinates remain real valued $x \to x$ but conjugated momenta become imaginary $p_x \to ip_x$) can be formulated as the following substitution for the wave function (cf. to (2))

$$\psi = A_E(X) \exp(-\gamma\sigma_E)\,, \tag{6}$$

where the action σ_E and we use the subscript E to denote so-called Euclidean action obtained from the WKB action σ after the Wick rotation. Performed above rotation is not a harmless change of variables. The deep meaning of this transformation within the instanton approach is related to redistribution of different terms between the Hamilton - Jacoby and the transport equations. Indeed, like that is in the WKB method, eigenvalues for the ground and for the low-lying states are of the order of γ^0, while all other terms in (3) are of the order of γ^1. Therefore to perform a regular expansion over γ^{-1} for the substitution (6) one has to remove the energy term from the Hamilton - Jacoby equation, and to include this term into the transport equation. Besides in the first order over γ^{-1} one can neglect the term with the second derivative of the prefactor. As a result of this redistributions the both equations are presented as

$$\frac{1}{2}\left(\frac{\partial\sigma_E}{\partial X}\right)^2 = V(X)\,, \tag{7}$$

instead of the WKB Hamilton - Jacoby equation (3), and the transport equation is

$$\frac{\partial A_E}{\partial X}\frac{\partial\sigma_E}{\partial X} + \frac{1}{2}\frac{\partial^2\sigma_E}{\partial X^2}A_E = \epsilon A_E\,. \tag{8}$$

One can easily note by a simple inspection of the WKB (3), (4) and of the instanton (7), (8) equations that although the both semiclassical methods

can be formulated neglecting terms of the order of γ^{-1}, therefore possessing the same accuracy over γ^{-1}, the solutions evidently coincide in the asymptotic classically forbidden region $V(X) \gg \epsilon/\gamma$, but their behavior, number and type of turning points (where any semiclassic approximation does not work) are quite different. For example in the WKB formalism there are two turning points where $V(X) - (\epsilon/\gamma) = 0$ around each minimum of the potential, while in the instanton approach since the energy does not enter the Hamilton - Jacoby equation (thus one can say that there are no classically accessible regions at all) the turning points are extremal points (minima for the case) of the potential. Furthermore as a consequence of this difference, in the WKB method all turning points are linear, whereas in the instanton approach they are second order (quadratic over X).

3 Accuracy of semiclassical approximation

Armed with this knowledge we are in the position now to construct our approximants. Let us introduce besides the comparison potential $V_c(X)$, one more specially chosen potential V_{sc} (henceforth will be referred to as the semiclassical potential). This potential is chosen by the requirement that the exact solutions to the Schrödinger equation with V_{sc} coincide asymptotically with the semiclassical solutions to the Schrödinger equation with the potential $V(X)$ the problem under study. Thus according to the construction, the semiclassical wave function Ψ_{sc} satisfies the equation

$$\Psi_{sc}^{-1}\frac{d^2\Psi_{sc}}{dX^2} = 2\gamma^2\left(V_{sc}(X) - \frac{\epsilon}{\gamma}\right), \tag{9}$$

and from here we can relate the semiclassical potential ($V_{sc}(X)$) with the bare one ($V(X)$)

$$V_{sc}^{(1,2)} = V(X) \mp \frac{1}{2\gamma^2}A^{-1}\left(\frac{d^2A}{dX^2}\right), \tag{10}$$

in the vicinity of the first order or of the second order (superscripts 1 or 2) turning points.

Since near the turning point X_0 the prefactors $A^{(1)} \propto |X - X_0|^{-1/4}$, and $A^{(2)} \propto (X - X_0)^n$ (where n is an integer number which occurs from the transport equation (8) solution at the energy $\epsilon = n + (1/2)$) the potential $V_{sc}^{(1)}$ at $X \to X_0$ is singular and negative, and $V_{sc}^{(2)}$ has the same singularity ($\propto (X - X_0)^{-2}$) but positive. The difference is due to the fact that near the

WKB linear turning points we have to deal with the $V_{sc}^{(1)}$ well, whereas near the second order instanton turning points one has to treat the potential barrier $V_{sc}^{(2)}$. It might be useful to illustrate the essential features of the introduced above potentials V_c and V_{sc} applying the definition (10) to a simple (but the generic touchstone) example of the following anharmonic oscillator

$$V(X) = \frac{1}{2}[X^2 + \alpha X^3 + \beta X^4]\,. \tag{11}$$

We show in Fig. 1 the semiclassical and the comparison potentials associated with (11) for the WKB (Fig. 1a) and instanton (Fig. 1b) methods ($\alpha = -1.25$, $\beta = 0.5$, and the energy window corresponds to $n = 3$ excited state of the potential (11)).

The key elements to construct our approximants are the following combinations related to probability flows to and from the turning points

$$\begin{aligned} J(X_1) &= \Psi_{sc}^{-1}\left(\frac{d\Psi_{sc}}{dX} - \Psi_c^{-1}\frac{d\Psi_c}{dX}\right)_{X=X_1} \qquad (12)\\ &= 2\gamma^2\Psi_{sc}^{-1}(X_1)\Psi_c^{-1}(X_1)\int_{-\infty}^{X_1}\Psi_{sc}(X)\Psi_c(X)(V_{sc}(X) - V_c(X))dX\,, \end{aligned}$$

where $X_1 < X_0$ and analogously for $X_2 > X_0$ the flow function $J(X_2)$ is given by (12) where the integration limits are from X_2 to $+\infty$. Since the exact wave functions are continuous with continuous first derivatives (providing due to these features the continuity of the density probability currents), the idea of our procedure is to require the same from the approximate wave functions.

The integrals entering $J(X_1)$ and $J(X_2)$ can be calculated easily for any form of the potential, and the maximum accuracy of the any semiclassical approach can be achieved upon the matching of the approximate solutions at the characteristic points $X_{1,2}^{\#}$ where $J(X_{1,2}^{\#}) = 0$. The points $X_{1,2}^{\#}$ do exist in the case when the potentials V_c and V_{sc} intersect in the region where the approximate wave functions Ψ_{sc} and Ψ_c are monotone ones. It is easy to realize (see e.g., Fig. 1) that the both points occur in the vicinity of the linear turning points for the potentials with $d^2V/dX^2 > 0$. One such a point disappears when the potential turning point becomes the inflection point, and there are no $X_{1,2}^{\#}$ points at all for $d^2V/dX^2 < 0$. In the vicinity of the second order turning point the comparison potential V_c is a parabolic one. The curvature of the latter potential can be always chosen to guarantee the two intersection points always exist. The choice of the comparison potential

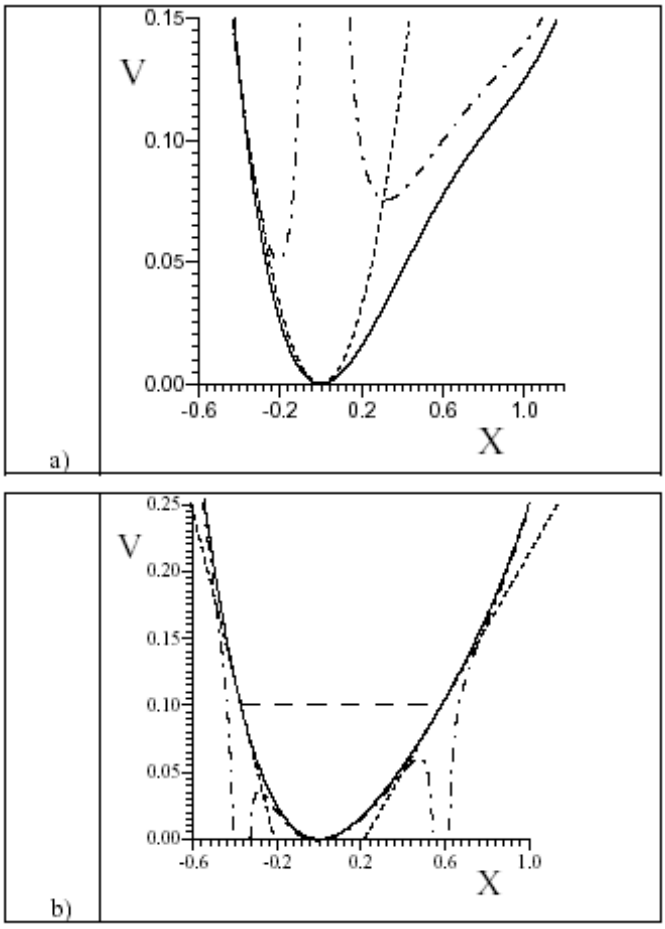

Figure 1: The characteristic semiclassical potentials V_{sc} (dot-dashed lines) and V_c (dashed lines) for the bare anharmonic potential (11): $\alpha = -1.25$, $\beta = 0.5$ ($\gamma = 33$, and the energy window corresponds to $n = 3$): (a) instanton approach; (b) WKB method.

corresponds to a certain renormalization ($\propto \gamma^{-2}$) of the characteristic oscillation frequency $(d^2V/dX^2)_{X=X_0}$. Note in passing that the approach we are advocating here conceptually close (although not identical) to the scale transformation proposed by Miller and Good [17] and further developed in [19].

Thus the conditions $J(X^{\#}_{1,2}) = 0$ allow us to construct well controlled approximate solutions to the Schrödinger equation. The accuracy of the

approximation depends on the deviation of the approximate wave functions from the exact ones in the vicinity of the characteristic points $X^{\#}_{1,2}$. In own turn, the deviation is determined by the higher over $(X - X_0)$ terms of the potential $V(X)$ which are not included in the harmonic comparison potential V_c. Include explicitely the corresponding higher order terms to distinguish V_c and V_{sc} potentials, we find in the vicinity of the linear turning points

$$V^{(1)}_{sc} - V_c \simeq -\frac{c_1}{\gamma^2}\,(X - X_0)^{-2} + \frac{\omega^2}{2}\,(X - X_0)^2\ , \tag{13}$$

where the universal numerical constant $c_1 = 5/32$, and the second term in the r.h.s. is related to deviation of the bare potential from the linear one. The same manner near the second order turning points

$$V^{(2)}_{sc} - V_c \simeq -\frac{c_2}{\gamma^2}\,(X - X_0)^{-2} + \alpha(X - X_0)^3\,, \tag{14}$$

where the universal constant $c_2 = n(n-1)/4$ is zero for the lowest vibrational states $n = 0\,,\ 1$, and the last term describes non-parabolicity of the potential. Note that unlike the semiclassical action which within the instanton method is independent of quantum numbers n, the position of the characteristic points does depend on n, and the $X^{\#}_{1,2}$ points are placed near the boundaries of the classically accessible region.

Now we are in the position to construct the approximate wave functions

$$\tilde{\Psi}(X) = \begin{cases} \Psi_c(X)\,,\ X^{\#}_1 < X < X^{\#}_2 \\ \Psi_{sc}\,,\ X < X^{\#}_1\,,\ X > X^{\#}_2 \end{cases}\ , \tag{15}$$

which are the solutions to the Schrödinger equation with the following piecewise smooth approximating potential

$$\tilde{V}(X) = \begin{cases} V_c(X)\,,\ X^{\#}_1 < X < X^{\#}_2 \\ V_{sc}\,,\ X < X^{\#}_1\,,\ X > X^{\#}_2 \end{cases}\ . \tag{16}$$

The wave functions calculated according to (15) in the framework of the instanton approach close to the Weber functions in the classically accessible regions, but their exponentially decaying tails in the classically forbidden regions correspond to the exact (bare) potential, not to its harmonic approximant. Analogously in the WKB method these functions (15) coincide with the semiclassical ones out of the interval $(X^{\#}_1\,,\ X^{\#}_2)$, and with the Airy functions in this interval.

To proceed further on we have to relate our approximate wave functions (15) and two linearly independent solutions to the bare Schrödinger equation Ψ_1 and Ψ_2. It can be written down formally as

$$\Psi(X) = \tilde{\Psi}(X) + \int_{X_0}^{X} dX' v(X') G(X, X') \Psi(X') \,, \tag{17}$$

where $v = V(X) - \tilde{V}(X)$, $G(X, X')$ is the Green function for the Schrödinger equation with the potential (16),

$$G(X, X_1) \equiv const[\tilde{\Psi}_1(X)\tilde{\Psi}_2(X_1) - \tilde{\Psi}_1(X_1)\tilde{\Psi}_2(X)] \,;\, X_1 \leq X \,, \tag{18}$$

where the constant in (18) is the Wronskian equal to $(2\gamma)^{-1}$ in the instanton method, and $i(2\gamma)^{-1}$ within the WKB approach. In (17) $\Psi \equiv (\Psi_1 \,,\, \Psi_2)$ (the same definition for $\tilde{\Psi}$), and we take the turning point X_0, where the functions Ψ and $\tilde{\Psi}$ are close to each other as the lower integration limit.

The solution to the integral equation (17) is expressed as the Neumann series expansion,

$$\Psi(X) = \tilde{\Psi}(X) + \int_{X_0}^{X} dX_1 v(X_1) G(X, X_1) \tilde{\Psi}(X_1) + \cdots \,, \tag{19}$$

and the m-th order term can be factorized and estimated as

$$\leq \frac{1}{m!} \left(\int_{X_0}^{X} dX_1 v(X_1) G(X, X_1) \tilde{\Psi}(X_1) \right)^m \,. \tag{20}$$

The integrals entering this estimation

$$\int_{X_0}^{X} dX_1 v(X_1) G(X, X_1) \tilde{\Psi}(X_1) = L_{12/22}(X) \tilde{\Psi}_1(X) + L_{11/21}(X) \tilde{\Psi}_2(X) \tag{21}$$

contain the 2×2 matrix with the following matrix elements

$$L_{ij} = \int_{X_0}^{X} dX' \tilde{\Psi}_i(X') v(X') \tilde{\Psi}_j(X') \,. \tag{22}$$

It is convenient to introduce the matrix $\hat{C}^{(n)}$ relating the n-th order wave function correction $\delta\Psi^{(n)}$ with the wave function $\tilde{\Psi}$

$$\begin{pmatrix} \delta\Psi_1^{(n)} \\ \delta\Psi_2^{(n)} \end{pmatrix} = \hat{C}^{(n)} \begin{pmatrix} \tilde{\Psi}_1 \\ \tilde{\Psi}_2 \end{pmatrix} \,, \tag{23}$$

and the full connection matrix between the exact and approximate wave functions

$$\begin{pmatrix} \Psi_1 \\ \Psi_2 \end{pmatrix} = \hat{C} \begin{pmatrix} \tilde{\Psi}_1 \\ \tilde{\Psi}_2 \end{pmatrix}, \tag{24}$$

is

$$\hat{C} = \sum_n \hat{C}^{(n)}. \tag{25}$$

According to the inequality (20)

$$\hat{C}^{(n)} \leq \frac{1}{n!}\hat{C}_0^n, \tag{26}$$

where

$$\hat{C}_0 = \begin{pmatrix} L_{12} & L_{11} \\ L_{22} & L_{12} \end{pmatrix}. \tag{27}$$

Combining finally the expressions (25) - (27) we end up with the upper and lower bounds for the correction matrix $\hat{C}$ estimation

$$1 + \hat{C}_0 \leq \hat{C} \leq \exp(\hat{C}_0). \tag{28}$$

We conclude from (20), (22) that the Neumann series posses an absolute convergence if all the matrix elements L_{ij} are finite. Besides, unlike the correction functions introduced within the Fröman approach [4], the integrals in (22) have no singularities on the real axis. Evidently the integrals (22) are finite with the oscillating WKB functions, since the perturbation potential $v(X)$ is not zero only in the close proximity to the characteristic points $X^{\#}_{1,2}$. However in the instanton method due to mixing of increasing and decreasing exponents, the matrix elements L_{22} is divergent. Despite of this divergency the product $L_{22}\tilde{\Psi}_1$, we are only interested in, is finite, and it is convenient to perform one more transformation to exclude explicitely this divergency.

Technically one can easily eliminate the both off-diagonal elements of the matrix $\hat{C}_0$ and thus to get rid of the divergency of the (exponentially decreasing solution $\tilde{\Psi}_1$) amplitude due to the contribution to the $\tilde{\Psi}_1$ the exponentially increasing solution $\tilde{\Psi}_2$. These linear transformations renormalize the correction matrix elements L_{22} and L_{11} as follows

$$L_{22}(X)\tilde{\Psi}_1(X) \equiv L^*_{22}(X)\tilde{\Psi}_2(X)\,;\; L_{11}(X)\tilde{\Psi}_2(X) \equiv L^*_{11}(X)\tilde{\Psi}_1(X), \tag{29}$$

where the renormalized matrix elements L^*_{22} and L^*_{11} read as

$$L^*_{22}(X) = \int_{X_0}^{X} dX' \frac{\tilde{\Psi}_1(X)\tilde{\Psi}_2(X')}{\tilde{\Psi}_1(X')\tilde{\Psi}_2(X)} \tilde{\Psi}_1(X')v(X')\tilde{\Psi}_2(X') \leq L_{12}(X)\,, \qquad (30)$$

and

$$L^*_{11}(X) = \int_{X_0}^{X} dX' \frac{\tilde{\Psi}_1(X')\tilde{\Psi}_2(X)}{\tilde{\Psi}_1(X)\tilde{\Psi}_2(X')} \tilde{\Psi}_1(X')v(X')\tilde{\Psi}_2(X') \geq L_{12}(X)\,. \qquad (31)$$

Now all the integrals entering L^*_{11}, L^*_{22}, and L_{12} are convergent and finite at any X, the correction matrix $\hat{C}_0$ is transformed into the diagonal and positively defined matrix $\hat{C}^*_0$

$$\hat{C}^*_0 = \begin{pmatrix} L^*_{11} - L_{12} & 0 \\ 0 & L_{12} - L^*_{22} \end{pmatrix}. \qquad (32)$$

The n-th order corrections in the instanton approach satisfy the inequality

$$0 \leq \delta\Psi^{(n)}_1 \leq (n!)^{-1}(L_{11} - L_{12})\tilde{\Psi}_1\,,\; 0 \leq \delta\Psi^{(n)}_2 \leq (n!)^{-1}(L_{12} - L^*_{22})\tilde{\Psi}_2\,. \quad (33)$$

Explicit summation of r.h.s in (33) gives us the upper and the lower bound limits for the solutions of the initial Schrödinger equation, i.e. the stripe where increasing and decreasing solutions are confined

$$\begin{aligned} |\tilde{\Psi}_1(X)| &\leq |\Psi_1(X)| \leq |\tilde{\Psi}_1(X)| \exp(L^*_{11} - L_{12})\,, \qquad (34) \\ |\tilde{\Psi}_2(X)| &\leq |\Psi_2(X)| \leq |\tilde{\Psi}_2(X)| \exp(L_{12} - L^*_{22})\,. \end{aligned}$$

It is our main result in this paper, and the stripe (34) gives the accuracy of the semiclassical instanton method. Besides we are in the position now to estimate the contribution of increasing semiclassical solutions into decreasing ones (what is relevant to solve eigenvalue problems). The summation convergent majorant series enables us to estimate the upper bound for this contribution

$$\frac{L^*_{11}}{L^*_{22}}\left(1 - \exp(-L_{12})\right)\,. \qquad (35)$$

Therefore at $L_{12} \ll 1$ the summation of all order perturbation terms enhances the 1-st order correction by the factor L_{12}/L^*_{22}. Analogously the majorant estimates described above can be used to construct the connection matrices linking the semiclassical solutions through the turning points. The comparison of the bare connection matrices (see e.g., [3, 9, 11, 13]) with the matrices calculated accordingly to (22) - (30) provides the estimates for the eigenvalue accuracy.

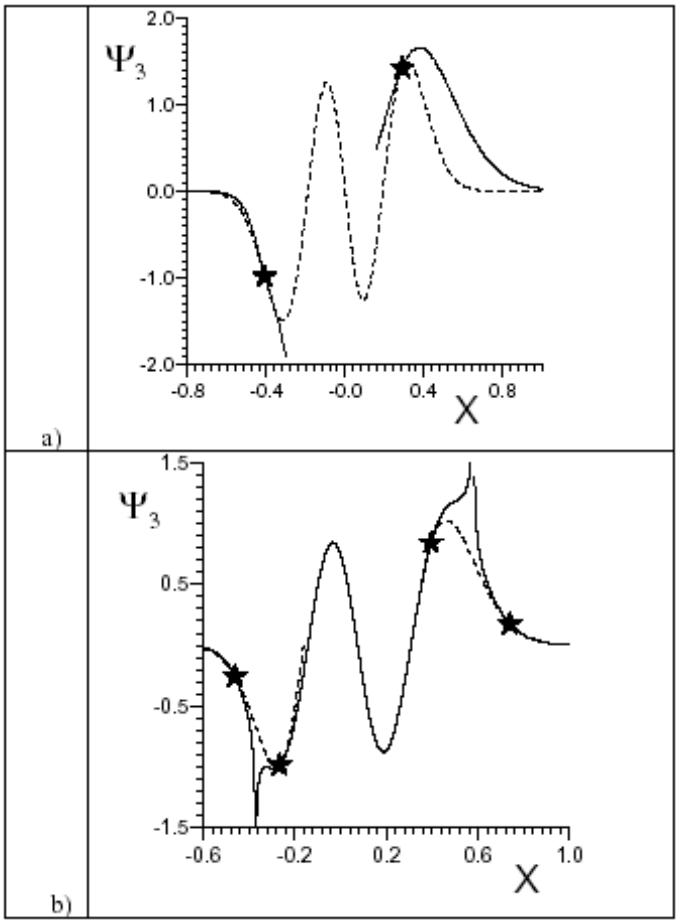

Figure 2: Semiclassical wave function Ψ_3 ($n = 3$) for the anharmonic potential (11) with $\alpha = -1.25$, $\beta = 0.5$ ($\gamma = 33$). Stars indicate the matching points, dashed lines show the solutions to the comparison equations, and: (a) - solid line traces the instanton solution; (b) - solid line shows the WKB wave function.

As it was mentioned already, for the WKB method the procedure is even more simple, since no any divergency and therefore no need to perform the transformation (29). The similar to (20) - (21) factorization gives the $\hat{C}_0$ matrix (cf. with (27) for the instanton approach)

$$\hat{C}_0 = i \begin{pmatrix} L_{12} & -L_{11} \\ L_{22} & -L_{12} \end{pmatrix} , \tag{36}$$

and the estimations for the n-th order contribution (cf. with (33)) can be formulated now as

$$|\hat{C}^{(2n)}| \leq \frac{1}{(2n)!} \begin{pmatrix} \Delta & 0 \\ 0 & \Delta \end{pmatrix}^n , \tag{37}$$

and

$$|\hat{C}^{(2n+1)}| \leq \frac{1}{(2n+1)!} \Delta^n \hat{C}_0 , \tag{38}$$

where we denote $\Delta \equiv L_{12}^2 - L_{11}L_{22}$. Correspondingly to (37), (38) the diagonal and off-diagonal correction matrix elements are bounded from above

$$|C_{11/22}| \leq \left| \cos\sqrt{\Delta} + iL_{12}\frac{\sin\sqrt{\Delta}}{\sqrt{\Delta}} \right| , \tag{39}$$

and

$$|C_{12/21}| \leq \left| L_{11}\frac{\sin\sqrt{\Delta}}{\sqrt{\Delta}} \right| . \tag{40}$$

The whole procedure we employed is rationalized in the Fig. 2, where we compare the solutions to the comparison equation with the anharmonic oscillator semiclassical wave functions computed within the instanton and WKB approaches and indicate the optimal matching points $X^{\#}$ found accordingly to the condition $J(X^{\#}) = 0$.

4 Anharmonic oscillator

In closing let us illustrate how our estimations (34), (37) - (40) work for a strongly anharmonic potential (11). Although it is not great triumph to re-derive the known results, our derivation illustrates several characteristic features of the correction matrix techniques derived in the Sect. 3: better accuracy, rapid convergence, simple disposal of divergences, and ease of computation in particular. The main message of our consideration in the precedent Sect. 3 is that the quantitative accuracy of the semiclassics depends crucially on the proximity of the semiclassical wave functions to the solutions of the comparison equation in the region of the asymptotically smooth matching. Therefore, it is tempting to improve the accuracy by taking into account the anharmonic corrections to the comparison potential $V_c(X)$. However, since the eigenvalues and the normalization of the wave functions are almost independent of the detailed behavior in the vicinity of the linear turning points (because near these points, situated at the

boundaries of the classically accessible region, the probability density (i.e. $|\Psi|^2$) is exponentially small) this idea is useless for the WKB approach. In contrast with this, for the instanton method, the accuracy can be improved considerably upon including the anharmonic corrections into the comparison potential. Indeed, within the instanton method the accuracy is determined by the vicinity of the second order turning points where the wave functions acquire the largest values (and just in this region the smooth matching described above has to be performed).

Let us remind first the traditional (but formulated within the semiclassical framework) perturbation theory. Keeping in the transport equation (4) the second derivative of the prefactor A, the system of the equations of Hamilton - Jacoby (3) and the exact transport equation

$$\frac{d^2A}{dX^2} - 2\gamma\left[\frac{dA}{dX}\frac{d\sigma}{dX} + \left(\frac{d^2\sigma}{dX^2} - \epsilon\right)A\right] = 0 \tag{41}$$

are exactly equivalent to the Schrödinger equation under consideration. For the second order turning points the anharmonic corrections

$$V_p = \frac{1}{2}\left(\alpha X^3 + \beta X^4\right) \tag{42}$$

can be considered as a perturbation and it is convenient to include this perturbation V_p into the transport equation (41). Then the comparison equation is reduced to the inhomogeneous Weber equation, and its solutions can be expanded over the Weber functions $D_\nu(X)$ [18] (see also [14, 15])

$$\Psi_\nu(X) = N_\nu\left(D_\nu(X) + \sum_k b_{k\nu}D_{\nu+k}(X)\right), \tag{43}$$

where $N_\nu^{-2} = 1 + \sum_k b_{\nu k}^2$ is the wave function normalization factor, the expansion coefficients are proportional to the small parameters $\alpha/\sqrt{\gamma}$, and β/γ, and the Weber function index ν is related to the energy eigenvalue $\epsilon = \nu + (1/2)$. This expansion (43) looks like a conventional perturbation series, but it does not. In the comparison equation we are keeping the both (decreasing and increasing) waves, and as a result of it, the indices of the Weber functions $\nu + k$ are not integer numbers. In the first order over the perturbation V_p the only non-zero coefficients in (43) correspond to the following selection rules

$$k = \pm 1, \pm 3\,;\ \text{and}\ k = 0, \pm 2, \pm 4 \tag{44}$$

for the cubic and fourth order anharmonic corrections respectively. Explicitely these non-zero expansion coefficients can be found by straitforward calculations, and they are

$$b_{0\nu} = -\frac{3}{2}\beta\left(\nu^2+\nu+\frac{1}{2}\right), b_{-1\nu} = -3\alpha\nu^2, b_{1\nu} = -\alpha(\nu+1), \quad (45)$$
$$b_{-2\nu} - \frac{\beta}{2}(\nu-1)\left(\nu-\frac{1}{2}\right), b_{2\nu} - \frac{\beta}{2}\left(\nu+\frac{3}{2}\right),$$

$$b_{-3\nu} = -\frac{1}{3}\alpha\nu(\nu-1)(\nu-2)(\nu-3), b_{3\nu} = -\frac{1}{3}\alpha,$$
$$b_{-4\nu} = -\frac{1}{4}\beta\nu(\nu-1)(\nu-2)(\nu-3)(\nu-4), b_{4\nu} = -\frac{1}{4}\beta.$$

On equal footing we can find the perturbative corrections to the Bohr-Sommerfeld quantization rules, and therefore the eigenvalues. The calculation is straightforward, though deserves some precaution and rather tedious. Skipping a large amount of tedious algebra we end up with the fractional part of the quantum number ν

$$\nu \equiv n + \chi_n, \quad (46)$$

and up to the second order over the anharmonic perturbation V_p we find

$$\chi_n^{(2)} = -\frac{15\alpha^2}{2\gamma}\left(n^2+n+\frac{11}{30}\right) + \frac{3\beta}{\gamma}\left(n^2+n+\frac{1}{2}\right). \quad (47)$$

However the described standard perturbative approach leads to qualitatively wrong features of the solutions. For example, the wave functions (43), (45) are represented as a product of ν independent exponential factors and dependent of ν polynomials. As it is well known [1] in one dimension the n-th excited state wave function must have n zeros (and the number of zeros may not be changed by any perturbation). However in the m-th order perturbation theory approximation, the wave function (43) corresponding to a certain excited state n contains Hermitian polynomials up to the order $n+3m$ or $n+4m$ for the cubic or quartic anharmonic perturbations, respectively. Therefore some false zeros of the wave function appears in the standard perturbation theory, and the region where the function oscillates becomes more and more wide in the higher order over perturbations approximation. The contributions of these qualitatively and quantitatively incorrect higher order terms become dominating in the asymptotic region

at $|\alpha\gamma| \sim 1$, $\beta\gamma \sim 1$. It conforms with the classical results due to Bender and Wu [20, 21] who have shown that for the quartic anharmonic potential ($\alpha = 0$, $\beta > 0$ in (11)) the convergency radius is zero. Moreover, for $\beta = 0$ and for an arbitrary small α (11) is the cubic anharmonic potential, i.e., the decay one. Thus it should have only complex eigenvalues, what is not the case for the eigenvalues calculated within the perturbation theory. The method we developed in Sect. 3 enables us not only to estimate more accurate the anharmonic corrections to the eigenvalues, and to bring the whole schema of the calculations in a more elegant form. Our finding of the correction matrices is not merely to surpass a technical difficulty of the standard perturbative method, it is more one of principle, and we will show that the method has no drawbacks of the perturbation theory.

The proof proceeds as follows. Let us consider first the instanton method for the anharmonic potential (41) possessing one second order turning point $X = 0$. As it was shown in the Sect. 3 one has to find also two other characteristic points which are the roots of the equation (12). We denote the points as $X_L^{\#}$, and $X_R^{\#}$ (to refer by the self-explanatory subscripts L and R to the left and to the right from the turning point $X = 0$). At the next step using the correction matrices introduced in the Sect. 3, we can define formally the transformation of our approximate wave functions (15) into the unknown exact wave functions Ψ as

$$\begin{pmatrix} \Psi_L \\ \Psi_R \end{pmatrix} = \hat{C} \begin{pmatrix} \tilde{\Psi}_L \\ \tilde{\Psi}_R \end{pmatrix}, \tag{48}$$

where as above the subscripts L and R refer to the wave functions in the regions to the left and to the right from the turning point $X = 0$. We do not know the correction matrix $\hat{C}$ but we do know (see (23) - (31)) the boundary estimations for the matrix.

The Eq. (48) can be used also to correct the known at the second order turning point the connection matrix $\hat{M}$ [3, 11, 13]. Indeed the connection matrices link the semiclassical solutions in the X-regions to the left and to the right from the turning points. For the isolated second order turning point (we are dealing within the instanton method), the connection matrix $\hat{M}$ links the exponentially increasing and decreasing solutions in the space regions separated by the turning point. The condition ensuring the correct asymptotic behavior is the quantization rule for this case which can be formulated as $M_{11} = 0$ (M_{ij} are the matrix elements of the connection matrix $\hat{M}$). Since in the regions to the left and to the right from the turning point our approximate solutions $\tilde{\Psi}$ coincide by their definition (15) with the semiclassical ones, the correction matrix method enables us to correct the

quantization rule too. Namely, the quantization rules are formulated within the connection matrix technique read now as

$$C_{22}^R T_2 C_{22}^L - C_{21}^R C_{21}^L \frac{\sin^2(\pi\nu)}{T_2} + (C_{22}^L C_{21}^R + C_{21}^L C_{22}^R)\cos(\pi\nu) = 0\,, \qquad (49)$$

where the Stokes constant for the second order turning point [3] is

$$T_2 = \frac{\sqrt{2\pi}}{\Gamma(-\nu)})\,, \qquad (50)$$

and $C_{ij}^{R,L}$ are the correction matrices at the $X_R^{\#}$ or $X_L^{\#}$ characteristic points respectively. Expanding the Gamma function entering (49) around the integer numbers, i.e., as above (46), $\nu = n + \chi_n$ one can find from the equation (49) the fractional part of the quantum number. If we were known the correction matrix $\hat{C}$ the solution of (49) would provide the exact eigenvalues. But we do know only the estimations from below and from above for the $\hat{C}$ matrix. In the same spirit we can calculate the estimations for the correction matrices (and therefore for the eigenvalues) within the WKB approach.

Luckily it turns out that the mathematical nature of the semiclassical problem is on our side here, and, in fact, even the first order estimation from below $\hat{C}^{(0)}$ (23) gives already the accuracy comparable with the standard perturbation procedure, and the estimation from above (25) gives the eigenvalues almost indistinguishable from the "exact" ones obtained by the numerical diagonalization of the Hamiltonian. The same true for the wave functions found by the correction matrix technique. We show in Fig. 3 $|\Psi_3|^2$ for the same anharmonic potential (11) with $\alpha = -1.25$, $\beta = 0.5$. Clearly the exact numerical results and those obtained by our correction matrix techniques are correct qualitatively and in the very good quantitative agreement (indistinguishable starting from the second order approximation) unlike the situation with the standard perturbation theory. Besides we present in the table the eigenvalues of the anharmonic potential. We take the anharmonic coefficients α and β in (11) so large, that corresponding perturbations of the eigen values are of the order of the bare harmonic frequency (one in our dimensionless units $\alpha = -1.2\,,\ \beta = 0.5$). In the table the eigenvalues found by the numerical diagonalization are presented in the column I. The column II contains the harmonic approximation results, the column III is the second order perturbation theory (47), and the columns IV and V results are obtained by applying our correction matrix technique: estimation from below with the first order correction matrix (23) in the column IV, and the estimation from above with the matrix (25) in the column V.

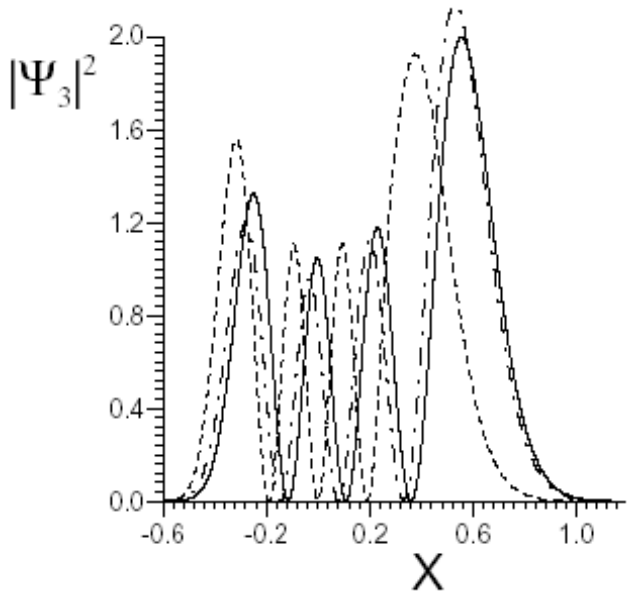

Figure 3: Comparison of the exact $|\Psi_3|^2$ (solid line) for the anharmonic potential (11) with $\alpha = -1.25$, $\beta = 0.5$ ($\gamma = 33$) with two lowest (zero and first order) approximations of the correction matrix method (dashed and dot-dashed lines). Note that the second order approximation with the relative accuracy 10^{-2} is indistinguishable from the exact numerical results.

Table 1: Eigenvalues of the anharmonic potential (11) ($\alpha = -1.2$, $\beta = 0.5$).

n =	I	II	III	IV	V
0	0.0149	0.0152	0.0149	0.0149	0.0149
1	0.0433	0.0455	0.0434	0.0433	0.0433
2	0.0697	0.0758	0.0701	0.0699	0.0695
3	0.0942	0.1061	0.0950	0.0946	0.0939
4	0.1168	0.1364	0.1182	0.1178	0.1162
5	0.1382	0.1667	0.1395	0.1396	0.1373

I the eigenvalues found by the numerical diagonalization;
II the harmonic oscillator eigenvalues;
III the eigenvalues in the second order perturbation theory (47);
IV the eigenvalues estimated from below by the correction matrix (23);
V the estimation from above with the matrix (25).

To conclude, as we have shown how to estimate the corrections to the main technical tool for the semiclassical approach, the connection matrices linking the solutions to the left and to the right from the turning points. Everything (e.g., the upper and the lower bounds for χ_n) is determined by the matrices L_{12} and L_{22}^*. Approximating to (11) potential is found from (13) and after that straightforward computing according to (22) the matrices L_{ij} and their renormalization (30) leads to the corrections we are looking for, presented in the Fig. 4, which allow us to estimate the accuracy of the semiclassical eigenstates and eigenfunctions. We conclude that even for a strongly anharmonic potential the both methods (WKB and instanton) are fairly accurate ones (about 5%) up to the energy close to the potential barrier top (in the region of negative curvature, we already discussed above).

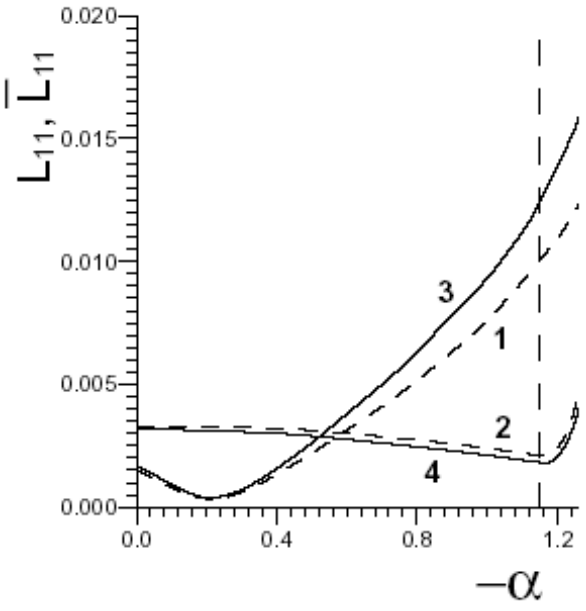

Figure 4: Corrections to the decreasing solutions in for the anharmonic potential (11); $\beta = 0.5$, $n = 3$, $\gamma = 33$; (1, 3) - instanton method, (2, 4) - WKB, (1, 2) - the first order corrections L_{11}, (3 , 4) - the upper bound estimation summing up all terms. The vertical dashed lines indicate the values of the cubic anharmonic term (α) where the inflection point and new extrema of the potential are appeared.

It is worth noting that in the frame work of the conventional perturbation theory (due to zero convergency radius with respect to β coefficient in (11)) pure computational problems to get the same accuracy become nearly unsurmountable, see e.g., [20, 22]. Our findings show that to estimate quantitatively the semiclassical accuracy it is enough to compare two linearly independent (with the same quantum number) solutions of the initial potential under study, and of the approximating piecewise smooth potential. The main advantage of the approach is related to the appropriate (13), (16) choice of the approximating potential, providing absolutely convergent majorant series (17) for the solutions. Actually our correction matrix technique is a fairly universal one and enables to estimate (and improve!) the semiclassical accuracy for arbitrary one dimensional potentials with any combination of the turning and of the crossing points.

We dedicate this paper in memoriam of our colleague and friend Dr. Israel Vagner.

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