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WKB corrections to the energy splitting in double well potentials

Marko Robnik†, Luca Salasnich‡ and Marko Vraničar†

†*Center for Applied Mathematics and Theoretical Physics, University of Maribor, Krekova 2, SI-2000 Maribor, Slovenia*

‡*Istituto Nazionale per la Fisica della Materia, Unità di Milano, Dipartimento di Fisica, Università di Milano, Via Celoria 16, I-20133 Milano, Italy*

E-mail: robnik@uni-mb.si, salasnich@mi.infm.it and mark.vranicar@uni-mb.si

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By using the WKB quantization we deduce an analytical formula for the energy splitting in a double–well potential which is the usual Landau formula with additional quantum corrections. Then we analyze the accuracy of our formula for the double square well potential, the inverted harmonic oscillator and the quartic potential.

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1 Introduction

Semiclassical quantization is very useful to understand the global behaviour of eigenfunctions and energy spectra of quantum systems, since it allows us to obtain analytic expressions. The leading semiclassical approximation (torus quantization) is just the first term of a certain $\hbar$–expansion, which is called WKB (Maslov and Fedoriuk 1981). A systematic study of the accuracy of semiclassical approximation is very important, especially in the context of quantum chaos (Casati and Chirikov 1995, Gutzwiller 1990). Since this is a difficult task, it has been attempted for simple systems, where in a few cases even exact solutions may be worked out (Bender, Olaussen and Wang 1977, Voros 1993, Robnik and Salasnich 1997a,b, Salasnich and Sattin 1997).

In this paper we analyze the energy splitting of doublets in a generic one–dimensional double–well potential. By using the WKB quantization we deduce an analytical formula for the energy splitting which is the usual Landau (1997) formula with additional quantum corrections. The splitting formula can be formally written as

$$\Delta E = A \exp\Big[-\frac{S}{\hbar}\Big], \tag{1}$$

where S is the usual classical action inside the classically forbidden region (between the two turning points) and A is called the tunneling amplitude, which can be written as a polynomial expression, expanded in powers of $\hbar$. This formula is based on a linear approximation of the potential near the turning points. First we introduce the basic definitions, then we derive in detail the splitting formula by using the semiclassical WKB expansion and finally we study its validity for the double square well potential, the inverted harmonic oscillator and the quartic potential. Our present work is essentially a semiclassical expansion theory of the tunneling amplitude A of equation (1). We shall demonstrate that it is indeed a significant improvement of the Landau approximation (1997). Also, we shall mention some potential applications.

2 Basic formalism

Let us consider a one–dimensional system with Hamiltonian

$$H = \frac{p^2}{2m} + V(x)\,, \tag{2}$$

where $V(-x) = V(x)$ is a symmetric double–well potential. The stationary Schrödinger equation of the system reads

$$\hat{H}\psi(x) = \Big(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\Big)\psi(x) = E\psi(x)\,. \tag{3}$$

The Sturm–Liouville theorem (see, for example, Courant and Hilbert 1968) ensures that for one–dimensional systems there are no degeneracies in the spectrum. Let ψ_1 and ψ_2 be two exact eigenfunctions of the Schrödinger equation

$$\hat{H}\psi_1 = E_1\psi_1 \quad \text{and} \quad \hat{H}\psi_2 = E_2\psi_2\,, \tag{4}$$

such that $\psi_1(-x) = \psi_1(x)$ and $\psi_2(-x) = -\psi_2(x)$ and $E_1 \simeq E_2$. To calculate the splitting $\Delta E = E_2 - E_1$, we multiply the first equation by ψ_2 and the second by ψ_1 and then we subtract the two resulting equations. By integrating from 0 to ∞ we find

$$\Delta E = \frac{\hbar^2}{2m}\frac{\psi_1(0)\psi'_2(0) - \psi'_1(0)\psi_2(0)}{\int_0^\infty \psi_1(x)\psi_2(x)dx}\,. \tag{5}$$

We write the eigenfunctions ψ_1 and ψ_2 in terms of the right–localized function

$$\psi_0(x) = \frac{1}{\sqrt{2}}(\psi_1(x) + \psi_2(x))\,. \tag{6}$$

It is easy to show that $E_0 = <\psi_0|\hat{H}|\psi_0> = \frac{1}{2}(E_1 + E_2)$. Then, with the approximation $\int_0^\infty \psi_0^2 dx \approx 1$, committing an exponentially small error, namely

$$\int_0^\infty \psi_1(x)\psi_2(x)dx = \int_0^\infty \psi_0^2(x)dx - \frac{1}{2} \approx \frac{1}{2}\,, \tag{7}$$

we get

$$\Delta E = \frac{2\hbar^2}{m}\psi_0(0)\psi'_0(0)\,, \tag{8}$$

which is an almost exact starting formula to calculate the energy splitting, since the error committed in approximation (7) is exponentially small. One should observe that this quantity is always positive, because the tail of the right localized eigenfunction $\psi_0(x)$ at $x = 0$ has the same sign for $\psi_0(0)$ and its derivative $\psi'_0(0)$. Another way to see this is to realize that due to the Sturm-Liouville theorem there are no degeneracies in one–dimensional systems, implying that all pairs of almost degenerate states, from the ground state up, are grouped by odd state above the even state.

3 Semiclassical method

To determine the function ψ_0 we perform a WKB expansion of the Schrödinger equation. We observe that a generic eigenfunction ψ of the Schrödinger equation can always be written as

$$\psi(x) = \exp\,(\frac{i}{\hbar}\sigma(x))\,, \tag{9}$$

where the phase $\sigma(x)$ is a complex function that satisfies the Riccati differential equation

$$\sigma'^2(x) + (\frac{\hbar}{i})\sigma''(x) = 2m(E - V(x))\,. \tag{10}$$

The WKB expansion for the phase is given by

$$\sigma(x) = \sum_{k=0}^{\infty}(\frac{\hbar}{i})^k\sigma_k(x)\,. \tag{11}$$

Substituting (11) into (10) and comparing like powers of $\hbar$ gives the recursion relation ($n > 0$) (see Bender, Olaussen and Wang 1977)

$$\sigma'_0{}^2 = 2m(E - V(x))\,, \quad \sum_{k=0}^{n}\sigma'_k\sigma'_{n-k} + \sigma''_{n-1} = 0\,. \tag{12}$$

With the momentum $p = \sqrt{2m(E - V(x))}$ the first five orders in the WKB expansion are given by

$$\sigma'_0 = p\,,$$

$$\sigma'_1 = -\frac{p'}{2p}\,,$$

$$\sigma'_2 = \frac{p''}{4p^2} - \frac{3}{8}\frac{p'^2}{p^3}\,,$$

$$\sigma_3' = \frac{p'''}{8p^3} + \frac{3}{4}\frac{p'p''}{p^4} - \frac{3}{4}\frac{p'^3}{p^5}\,,$$

$$\sigma_4' = \frac{1}{16}\left(\frac{p''''}{p^4} - 10\frac{p'''p'}{p^5} - \frac{13}{2}\frac{p''^2}{p^5}\right) + \frac{1}{16}\left(\frac{99}{2}\frac{p''p'^2}{p^6} - \frac{297}{8}\frac{p'^4}{p^7}\right), \qquad (13)$$

$$\sigma_5' = \frac{1}{32}\left(-\frac{p'''''}{p^5} + 15\frac{p''''p'}{p^6} + 24\frac{p'''p''}{p^6}\right) + \frac{1}{32}\left(-111\frac{p'''p'^2}{p^7} - 144\frac{p''^2p'}{p^7}\right) + \frac{1}{32}\left(510\frac{p''p'^3}{p^8} - 306\frac{p'^5}{p^9}\right).$$

In particular, if we call a and b the two turning points corresponding to the energy E, the right localized wavefunction ψ_0 is given by

$$\psi_0(x) = \frac{C_1}{\sqrt{|p|}}\exp\left[\frac{i}{\hbar}\left(\int_a^x |p|\,dx + \sigma_{even}\right) + \frac{1}{\hbar}\sigma_{odd}\right] + \frac{C_2}{\sqrt{|p|}}\exp\left[-\frac{i}{\hbar}\left(\int_a^x |p|\,dx + \sigma_{even}\right) + \frac{1}{\hbar}\sigma_{odd}\right], \qquad (14)$$

for $a < x < b$ (allowed region), where

$$\sigma_{even} = \sum_{k=1}^{\infty}(-1)^k\hbar^{2k}\sigma_{2k}(|p(x)|) \quad \text{with} \;\; \sigma_{2k}(-|p|) = -\sigma_{2k}(|p|)\,, \qquad (15)$$

and

$$\sigma_{odd} = \sum_{k=1}^{\infty}(-1)^k\hbar^{2k+1}\sigma_{2k+1}(|p(x)|) \quad \text{with} \;\; \sigma_{2k+1}(-|p|) = \sigma_{2k+1}(|p|)\,. \qquad (16)$$

Instead we get

$$\psi_0(x) = \frac{C_a}{\sqrt{|\tilde{p}|}}\exp\left[\frac{1}{\hbar}\left(\int_a^x |\tilde{p}|\,dx + \tilde{\sigma}_{even} + \tilde{\sigma}_{odd}\right)\right], \qquad (17)$$

for $x < a$ (forbidden region), and also

$$\psi_0(x) = \frac{C_b}{\sqrt{|\tilde{p}|}}\exp\left[\frac{1}{\hbar}\left(-\int_b^x |\tilde{p}|\,dx - \tilde{\sigma}_{even} + \tilde{\sigma}_{odd}\right)\right], \qquad (18)$$

for $b < x$ (forbidden region), where

$$\tilde{\sigma}_{even} = \sum_{k=1}^{\infty}\hbar^{2k}\tilde{\sigma}_{2k}(|\tilde{p}(x)|) \quad \text{with} \;\; \tilde{\sigma}_{2k}(-|\tilde{p}|) = -\tilde{\sigma}_{2k}(|\tilde{p}|)\,, \qquad (19)$$

and

$$\tilde{\sigma}_{odd} = \sum_{k=1}^{\infty}\hbar^{2k+1}\tilde{\sigma}_{2k+1}(|\tilde{p}(x)|) \quad \text{with} \;\; \tilde{\sigma}_{2k+1}(-|\tilde{p}|) = \tilde{\sigma}_{2k+1}(|\tilde{p}|)\,, \qquad (20)$$

where $\tilde{p} = \sqrt{2m(V(x)-E)}$ and $\tilde{\sigma}_k'(x) = \sigma_k'(\tilde{p}(x))$. In evaluating the integrals σ_k using (13) we cannot integrate naively on the real axis, because such integrals are divergent, but must take a partial derivative w.r.t. the energy of certain fundamental complex contour integral. See (Bender *et al* 1977) and section 6.

We observe that it is possible to write C_a, C_b, C_1 and C_2 in terms of a unique parameter C by imposing the uniqueness of the wavefunction ψ_0 at the turning points. Following Landau (1997) and Merzbacher (1970) we suppose that near the turning point $x = a$ it is possible to approximate the potential locally linearly by writing

$$E - V(x) = F_0(x-a)\,, \qquad (21)$$

with $F_0 > 0$. In this case the connections at the turning point imply that

$$C_a = C_b = C\,, \;\; C_1 = Ce^{i\frac{\pi}{4}}\,, \;\; C_2 = Ce^{-i\frac{\pi}{4}}\,, \qquad (22)$$

and the right localized function $\psi_0(x)$ can be written for $|x| < a$ as

$$\psi_0(x) = \frac{C}{\sqrt{|\tilde{p}|}}\exp\left[\frac{1}{\hbar}\left(\int_a^x |\tilde{p}|\,dx + \tilde{\sigma}_{even} + \tilde{\sigma}_{odd}\right)\right]. \qquad (23)$$

In this way the splitting formula, up to the 5th order, after taking into account some straightforward relations for σ_k and its derivatives (see the Appendix), becomes

$$\begin{aligned}\Delta E &= \frac{2\hbar C^2}{m}\Big[\,1+\hbar 2\tilde\sigma_2(0)+\hbar^2 2\tilde\sigma_2^2(0)\\ &\quad+\hbar^3\left(2\tilde\sigma_4(0)+\frac{4}{3}\tilde\sigma_2^3(0)\right)\\ &\quad+\hbar^4\left(\frac{2}{3}\tilde\sigma_2^4(0)+4\tilde\sigma_2(0)\tilde\sigma_4(0)\right)\Big] \qquad (24)\\ &\quad\times\exp\left[-\frac{2}{\hbar}\int_0^a|\tilde p|\,dx\right].\end{aligned}$$

The equation (24) can be written in a compact form, certainly up to the 5th order, and probably also generally to all orders, as follows

$$\Delta E=\frac{2\hbar C^2}{m}\exp\left[\frac{2}{\hbar}\left(-\int_0^a|\tilde p|\,dx+\tilde\sigma_{even}(0)\right)\right]; \qquad (25)$$

$$\tilde\sigma_{even}(0)=\int_a^0\tilde\sigma'_{even}(|\tilde p(x)|)\,dx\,.$$

To determine C we impose the normalization condition

$$1=\int_0^\infty|\psi_0(x)|^2dx\,, \qquad (26)$$

from which we get

$$2C^2\int_a^b\frac{1}{p}\exp\left(2\frac{\sigma_{odd}}{\hbar}\right)dx=1\,, \qquad (27)$$

and an expression for C^2,

$$\begin{aligned}C^2 &= \frac{1}{2}\left[\int_a^b\frac{1}{p}\,dx\right]^{-1}\left\{1+2\hbar^2\frac{\int_a^b\frac{\sigma_3}{p}\,dx}{\int_a^b\frac{1}{p}\,dx}\right.\\ &\quad\left.+2\hbar^4\left(2\left[\frac{\int_a^b\frac{\sigma_3}{p}\,dx}{\int_a^b\frac{1}{p}\,dx}\right]^2-\frac{\int_a^b\frac{\sigma_3^2+\sigma_5}{p}\,dx}{\int_a^b\frac{1}{p}\,dx}\right)\right\},\end{aligned} \qquad (28)$$

which is valid up to the 4th order in the $\hbar$ power series of C^2. The final formula is given by

$$\begin{aligned}\Delta E &= \frac{\hbar}{m}\left[\int_a^b\frac{1}{p}\,dx\right]^{-1}\\ &\quad\times\left\{1+2\hbar\tilde\sigma_2(0)+2\hbar^2\left(\tilde\sigma_2^2(0)+\frac{\int_a^b\frac{\sigma_3}{p}\,dx}{\int_a^b\frac{1}{p}\,dx}\right)\right.\\ &\quad+2\hbar^3\left(\tilde\sigma_4(0)+\frac{2}{3}\tilde\sigma_2^3(0)+2\tilde\sigma_2(0)\frac{\int_a^b\frac{\sigma_3}{p}\,dx}{\int_a^b\frac{1}{p}\,dx}\right)\\ &\quad+2\hbar^4\left(\frac{1}{3}\tilde\sigma_2^4(0)+2\tilde\sigma_2(0)\tilde\sigma_4(0)\right)\\ &\quad+2\hbar^4\left(2\tilde\sigma_2^2(0)\left[\frac{\int_a^b\frac{\sigma_3}{p}\,dx}{\int_a^b\frac{1}{p}\,dx}\right]\right) \qquad (29)\\ &\quad\left.+2\hbar^4\left(2\left[\frac{\int_a^b\frac{\sigma_3}{p}\,dx}{\int_a^b\frac{1}{p}\,dx}\right]^2-\frac{\int_a^b\frac{\sigma_3^2+\sigma_5}{p}\,dx}{\int_a^b\frac{1}{p}\,dx}\right)\right\}\\ &\quad\times\exp\left[-\frac{2}{\hbar}\int_0^a|\tilde p|\,dx\right].\end{aligned}$$

This formula is the usual Landau (1997) formula for the energy splitting (1st order in $\hbar$ for the tunneling amplitude) with additional quantum corrections (up to the 5th order in $\hbar$ for the tunneling amplitude). We note that higher–order WKB corrections quickly increase in complexity (Robnik and Salasnich 1997a,b) but, in principle, they can be calculated from the equation (12). It is important to stress that our splitting formula is good if the potential is sufficiently smooth so that the linear approximation is valid near the turning points.

The same splitting formula (25) and (29) can be derived using the semiclassical scattering formalism, for example as expounded by Iyer and Will (1987) and by Will and Guinn (1988). However, the main result (25) and (29) of this paper cannot be obtained by simple substitution or reinterpretation of their results. They use the scattering approach and treat the scattering problem (asymptotical free motion), calculating the transmission coefficients for the tunneling penetration through a potential barrier, and specifically they treat the

behaviour near to the top of the potential barrier. Also, their approach is doubly perturbative, namely they make the power expansion of the potential around the top of the barrier whose leading term is of course the inverted harmonic oscillator plus power terms in the series expansion, and they do at the same time the semiclassical expansion in terms of the powers of the Planck constant $\hbar$. They offer a formalism (an algorithm) how to calculate the requested quantities (transmission coefficients) to all orders, however they solve the relevant equation only up to the fourth order. So, their result cannot be easily mapped (by substitutions and other simple operations) onto our problem and our solution. Indeed, to get the result (25) and (29) using the scattering approach it is necessary to go back to the very first step in their formalism.

We have done this and confirmed, as mentioned above, that the result is the same. To this end the solution is written down in the form of the semiclassical ansatz in each of five regions separated by the turning points. At the turning points we do not request the condition of the continuity of the wavefunction and its derivative, but use the so-called Kramers correspondence rules instead (they determine the coefficients of the ansatz in such a way, that exponentially increasing solution in the classically forbidden regions does not occur). Thus, the asymptotic boundary conditions for the scattering problem are automatically taken into account: no propagation to the left or to the right of the classically allowed region.

Using this ansatz we have six unknown coefficients plus the eigenenergy that we seek, and we have six linear equations plus the normalization condition, so the problem is well defined. This system of equations can be reduced by simple elimination of some of the coefficients to a set of two homogeneous linear equations for which the solvability condition is now vanishing of its determinant, which must be satisfied precisely at the eigenvalues of the energy. Assuming that the pair of almost degenerate levels is separated by a small amount ΔE, we can do the Taylor expansion up to the first order in ΔE, neglect the quadratic and higher terms, and obtain exactly the equation (25) and (29).

4 Double square well potential

As the first example, we consider the double square well potential. In this case the linear approximation of the potential near the turning point is not valid. The potential is given by

$$V(x) = \begin{cases} V_0 & \text{for } |x| < a \\ 0 & \text{for } a < |x| < b \\ \infty & \text{for } |x| > b \end{cases} \qquad (30)$$

For this potential we have $p'(x) = p''(x) = 0$ for $-a < x < a$ and the corrections to the Landau (1997) formula are zero. A naive application of the splitting formula gives

$$\Delta E = \frac{2\hbar\sqrt{E}}{\sqrt{2m}(b-a)} \exp\Big(-\frac{2a}{\hbar}\sqrt{2m(V_0-E)}\Big)\,. \qquad (31)$$

This formula is *not* correct. In fact, by using the exact[1] wavefunction

$$\psi_0(x) = D\exp\Big(-\frac{1}{\hbar}\sqrt{2m(V_0-E)}x\Big) \qquad (32)$$

for $0 < x < a$ (forbidden region), and

$$\psi_0(x) = A\exp\Big(\frac{i}{\hbar}\sqrt{2mE}x\Big) + B\exp\Big(-\frac{i}{\hbar}\sqrt{2mE}x\Big) \qquad (33)$$

for $a < x < b$ (allowed region), and by imposing the exact matching and normalization conditions (Flügge 1971) we find

$$A = \frac{D}{2}\left(1 - i\sqrt{\frac{V_0-E}{E}}\right) \times \exp\Big(\frac{a}{\hbar}\sqrt{2m(V_0-E)} - \frac{a}{\hbar}\sqrt{E}\Big)\,, \qquad (34)$$

[1] Actually, strictly speaking, this is not exact but nevertheless the same expression that we get by evaluating the leading term for ΔE by using the implicit trigonometric eigenvalue equation (Flügge 1971, Robnik and Salasnich 1997, unpublished).

$$B = \frac{D}{2}\left(1+i\sqrt{\frac{V_0-E}{E}}\right) \times \exp\left(\frac{a}{\hbar}\sqrt{2m(V_0-E)}+\frac{a}{\hbar}\sqrt{E}\right), \quad (35)$$

and

$$D^2 = \frac{2E}{V_0(b-a)}\exp\Big(-\frac{2a}{\hbar}\sqrt{2m(V_0-E)}\Big). \quad (36)$$

Then we obtain:

$$\Delta E = \frac{4\hbar E\sqrt{2m(V_0-E)}}{mV_0(b-a)} \times \exp\Big(-\frac{2a}{\hbar}\sqrt{2m(V_0-E)}\Big). \quad (37)$$

This is the exact energy splitting for the double square well potential. It differs by a factor $4\sqrt{E(V_0-E)}/V_0$ from the WKB result based on the connection formulae (21–22) which are not justified in the present case.

5 Inverted harmonic oscillator

In this section we compare the Landau formula of the energy splitting with the exact one. We consider the inverted harmonic oscillator given by

$$V(x) = \begin{cases} V_0(1-\frac{x^2}{a^2}) & \text{for } |x|<a \\ 0 & \text{for } a<|x|<b \\ \infty & \text{for } |x|>b \end{cases} \quad (38)$$

We can introduce the following reduced variables

$$\bar{x}=\frac{x}{a}\,,\quad \bar{b}=\frac{b}{a}\,,\quad \bar{E}=\frac{E}{V_0}\,,\quad \hbar_{eff}=\frac{\hbar}{a\sqrt{mV_0}}\,. \quad (39)$$

Then it is not difficult to show that the Landau formula reads

$$\Delta\bar{E} = 2\hbar_{eff}D^2\exp\Big(-\frac{\pi}{\hbar_{eff}\sqrt{2}}(1-\bar{E})\Big), \quad (40)$$

where

$$D^2 = \Big[\frac{1}{2}\ln\Big(\frac{1+\sqrt{\bar{E}}}{1-\sqrt{\bar{E}}}\Big)+\frac{(\bar{b}-1)}{\sqrt{\bar{E}}}\Big]^{-1}. \quad (41)$$

This formula can be compared with the exact energy splitting. Let $\psi(x)$ be a quantum state of the inverted harmonic oscillator. It can be written in terms of the eigenstates $\psi^{(+)}$ and $\psi^{(-)}$ of the square well potential

$$\psi(x) = \sum_{n=1}^{\infty}(a_n\psi_n^{(+)}+b_n\psi_n^{(-)}),, \quad (42)$$

where

$$\psi_n^{(+)} = \frac{1}{\sqrt{b}}\cos\left[\pi\frac{2n-1}{2b}x\right],$$
$$\psi_n^{(-)} = \frac{1}{\sqrt{b}}\sin\left[\pi\frac{n}{b}x\right].$$

The matrix elements of the quantum Hamiltonian of the inverted harmonic oscillator read

$$H_{m,n}^{(+)} = \int_{-b}^{b}\psi_m^{(+)}\hat{H}\psi_n^{(+)}\,dx =$$

$$= \begin{cases} m=n: & \frac{\hbar_{ef}^2}{2}\left(\frac{2n-1}{2b}\pi\right)^2+\frac{2}{3b} \\ & +\frac{2b^2}{\pi^3(2n-1)^3}\sin\left[\frac{2n-1}{b}\pi\right] \\ & -\frac{2b}{(2n-1)^2\pi^2}\cos\left[\frac{2n-1}{b}\pi\right] \\ m\neq n: & \frac{2b^2}{\pi^3}\left(\frac{\sin\left[\frac{m-n}{b}\pi\right]}{(m-n)^3}+\frac{\sin\left[\frac{m+n-1}{b}\pi\right]}{(m+n-1)^3}\right) \\ & -\frac{2b}{\pi^2}\left(\frac{\cos\left[\frac{m-n}{b}\pi\right]}{(m-n)^2}+\frac{\cos\left[\frac{m+n-1}{b}\pi\right]}{(m+n-1)^2}\right), \end{cases} \quad (43)$$

and

$$H_{m,n}^{(-)} = \int_{-b}^{b}\psi_m^{(-)}\hat{H}\psi_n^{(-)}\,dx =$$

$$= \begin{cases} m=n: & \frac{\hbar_{ef}^2}{2}\left(\frac{n}{b}\pi\right)^2+\frac{2}{3b} \\ & -\frac{2b^2}{\pi^3(2n)^3}\sin\left[\frac{2n}{b}\pi\right] \\ & +\frac{2b}{(2n)^2\pi^2}\cos\left[\frac{2n}{b}\pi\right] \\ m\neq n: & \frac{2b^2}{\pi^3}\left(\frac{\sin\left[\frac{m-n}{b}\pi\right]}{(m-n)^3}-\frac{\sin\left[\frac{m+n}{b}\pi\right]}{(m+n)^3}\right) \\ & -\frac{2b}{\pi^2}\left(\frac{\cos\left[\frac{m-n}{b}\pi\right]}{(m-n)^2}-\frac{\cos\left[\frac{m+n}{b}\pi\right]}{(m+n)^2}\right). \end{cases} \quad (44)$$

The exact energy splitting is obtained by numerical diagonalization, in quadruple precision, of the

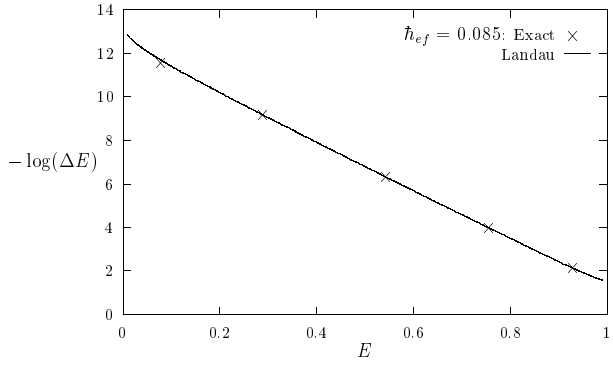

Figure 1: Negative logarithm of $\Delta\bar{E}$ *vs* mean energy $\bar{E}$ of pairs of almost degenerate consecutive energy levels. Inverted harmonic oscillator with $\hbar_{eff} = 0.085$ and $b = 1.5$.

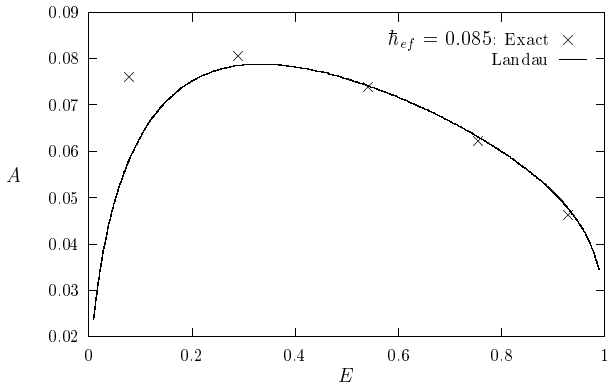

Figure 2: Tunneling amplitude A *vs* mean energy $\bar{E}$ of pairs of almost degenerate consecutive energy levels. Inverted harmonic oscillator with $\hbar_{eff} = 0.085$ and $b = 1.5$.

quantum Hamiltonian. We took a 4800×4800 matrix, thereby achieving 31 valid digits for the lower levels that we consider. In figure 1 we plot the negative logarithm of $\Delta\bar{E}$ as a function of the mean energy $\bar{E}$ of pairs of almost degenerate consecutive energy levels. We note a very good agreement between the exact and the Landau splittings. To resolve the differences, in figure 2 we show the tunneling amplitude A (= the expression (29) without the exponential tunneling factor) as a function of the mean energy $\bar{E}$ of pairs of almost degenerate consecutive energy levels.

6 Quartic potential

In this section we consider the well known quartic potential, given by

$$V(x) = -2Bx^2 + Ax^4\,, \tag{45}$$

where the parameters A and B are related to the potential barrier V_0 and to the position of the minimum x_0 by

$$V_0 = \frac{B^2}{A}, \quad x_0 = \sqrt{\frac{B}{A}}\,. \tag{46}$$

By using the following reduced variables

$$\bar{x} = \frac{x}{x_0}\,, \quad \bar{E} = \frac{E}{V_0}\,, \quad \hbar_{eff} = \frac{\hbar}{x_0\sqrt{mV_0}}\,, \tag{47}$$

the quantum Hamiltonian operator of the system can be written

$$\hat{H} = -\frac{\hbar_{eff}^2}{2}\frac{\partial^2}{\partial\bar{x}^2} - 2\bar{x}^2 + \bar{x}^4\,. \tag{48}$$

Let $|\psi\rangle$ be a state of the quartic potential. It can be written in terms of the eigenstates $|n\rangle$ of the harmonic oscillator

$$|\psi\rangle = \sum_{n=0}^{\infty} c_n|n\rangle\,. \tag{49}$$

The Schrödinger equation for the harmonic oscillator is

$$-\frac{\hbar_{ef}^2}{2}\frac{\partial^2|n\rangle}{\partial x^2} + \frac{\omega^2}{2}x^2|n\rangle = E_n|n\rangle\,. \tag{50}$$

By introducing the creation and annihilation operators

$$\hat{a}^+ = \frac{1}{\sqrt{2\hbar_{ef}\omega}}(\omega x - i\hat{p})\,,$$

$$\hat{a} = \frac{1}{\sqrt{2\hbar_{ef}\omega}}(\omega x + i\hat{p})\,, \tag{51}$$

which have the following properties

$$\hat{a}^+|n\rangle = \sqrt{n+1}|n+1\rangle\,,$$

$$\hat{a}|n\rangle = \sqrt{n}|n-1\rangle\,, \tag{52}$$

we get the matrix elements of the quantum Hamiltonian of the quartic potential

$$\begin{aligned} H_{n,m} &= \langle n|\hat{H}|m\rangle \\ &= \delta_{n,m}\left(\hbar_{ef}\left(\frac{\omega}{4}-\frac{1}{\omega}\right)(2n+1)\right) \\ &\quad +\delta_{n,m}\left(\frac{3\hbar_{ef}^2}{4\omega^2}(2n^2+2n+1)\right) \\ &\quad +\delta_{n+2,m}\sqrt{(n+1)(n+2)} \\ &\quad \times\left(-\hbar_{ef}\left[\frac{\omega}{4}+\frac{1}{\omega}\right]+\frac{\hbar_{ef}^2}{2\omega^2}(2n+3)\right) \\ &\quad +\delta_{n+4,m}\left(\frac{\hbar_{ef}^2}{4\omega^2}\right) \\ &\quad \times\sqrt{(n+4)(n+3)(n+2)(n+1)}\,. \end{aligned} \tag{53}$$

We calculate numerically, in quadruple precision (32 decimal digits), the energy levels of the system in the basis of the harmonic oscillator. For numerical purposes we took $\omega = 2$ and the dimensionality 1000×1000, thereby again achieving 31 valid digits for the lower levels that we consider.

In this way we can compare the exact energy splittings with the semiclassical ones, which are obtained by using our splitting formula (29). For the quartic potential we have

$$\begin{aligned} \tilde{\sigma}_0(0) &= -\sqrt{2}\int_0^a \sqrt{V(x)-E}\,dx \\ &= \frac{2\sqrt{2}}{3}\left[\frac{b^2+E}{b}\mathrm{F}(k)-b\mathrm{E}(k)\right], \\ \tilde{\sigma}_2(0) &= -\frac{1}{24\sqrt{2}}\frac{\partial}{\partial E}\int_0^a \frac{V''\,dx}{\sqrt{V(x)-E}} \\ &= \frac{1}{24\sqrt{2}a^2b}\left[\frac{(2+3E)b^2+E}{\sqrt{1+E}\,b^4}\mathrm{F(k)}\right. \\ &\quad \left.-\frac{1+3E}{1+E}\mathrm{E(k)}\right], \end{aligned} \tag{54}$$

$$\begin{aligned} \tilde{\sigma}_4(0) &= -\frac{1}{1152\sqrt{2}}\left[\frac{\partial^2}{\partial E^2}\int_0^a \frac{V''''\,dx}{\sqrt{V(x)-E}}\right. \\ &\quad \left.-\frac{7}{5}\frac{\partial^3}{\partial E^3}\int_0^a \frac{V''^2\,dx}{\sqrt{V(x)-E}}\right] \\ &= -\frac{1}{48\sqrt{2}}\left[Z_1\mathrm{F(k)}+Z_2\mathrm{E(k)}\right], \end{aligned}$$

where

$$a=\sqrt{1-\sqrt{1+E}},\quad b=\sqrt{1+\sqrt{1+E}},\quad k=\frac{a^2}{b^2}.$$

Moreover we get

$$\begin{aligned} \int_a^b \frac{1}{p}\,dx &= \frac{1}{\sqrt{2}}\frac{\mathrm{F}(m)}{b}, \\ \int_a^b \frac{\sigma_3}{p}\,dx &= \frac{1}{48\sqrt{2}}\frac{\partial^2}{\partial E^2}\int_a^b \frac{V''}{\sqrt{E-V}}\,dx \\ &= -\frac{1}{12\sqrt{2}}\left[K_1\mathrm{F}(m)+K_2\mathrm{E}(m)\right], \end{aligned} \tag{55}$$

$$\begin{aligned} \int_a^b \frac{\sigma_3^2+\sigma_5}{p}\,dx &= \frac{1}{2304\sqrt{2}}\left[\frac{7}{5}\frac{\partial^4}{\partial E^4}\int_a^b \frac{V''^2\,dx}{\sqrt{E-V}}\right. \\ &\quad \left.-\frac{\partial^3}{\partial E^3}\int_a^b \frac{V''''\,dx}{\sqrt{E-V}}\right] \\ &= \frac{1}{1440\sqrt{2}}\left[Q_1\mathrm{F}(m)+Q_2\mathrm{E}(m)\right], \end{aligned}$$

where $m = \frac{b^2-a^2}{b^2}$, and the functions $\mathrm{F}(m)$ and $\mathrm{E}(m)$ are the complete elliptic integrals of 1st and 2nd kind, respectively, defined by (Abramowitz and Stegun 1972)

$$F(m)=\int_0^1 \frac{dx}{\sqrt{(1-x^2)(1-mx^2)}}, \tag{56}$$

$$E(m)=\int_0^1 \frac{\sqrt{1-mx^2}}{\sqrt{1-x^2}}dx\,. \tag{57}$$

The functions Z_1, Z_2, K_1, K_2, Q_1 and Q_2 are defined as follows:

$$
\begin{aligned}
Z_1 &= -\frac{1}{480(1+E)^3a^6b^5} \\
&\times \Big(56b^2+135Eb^2+810E^2b^2-165E^3b^2 \\
&\quad +112+333E-1050E^2-375E^3\Big)\,, \\
Z_2 &= \frac{224+603E+570E^2-705E^3}{480(1+E)^3a^6b^5}\,, \\
K_1 &= -\frac{(1-7E)}{16(1+E)^2a^2b^3}\,, \\
K_2 &= \frac{4+5E+9E^2}{16(1+E)^2a^4b^3}\,,
\end{aligned}
\tag{58}
$$

$$
\begin{aligned}
Q_1 &= -\frac{1}{128(1+E)^{9/2}a^6b^9} \\
&\times \Big(b^2\Big(672+2263E+2730E^2+9595E^3 \\
&\quad -2008E^4-1136E^5-528E^6\Big) \\
&\quad +\Big(728E+2454E^2+3755E^3 \\
&\quad +11008E^4-349E^5+528E^6\Big)\Big)\,, \\
Q_2 &= \frac{3(56+209E+289E^2+195E^3-165E^4)}{8(1+E)^4a^8b^7}\,.
\end{aligned}
$$

In most of the above manipulations we have used the Mathematica software. Please note that the quantities (13) needed in (29) are strongly divergent at the turning points, but all the expressions in (29) can be made finite by taking partial derivatives with respect to E of certain finite expressions as in (54) and (55), implying that in our formula (25) then all quantities are convergent and finite (c.f. Bender *et al* 1977, Robnik and Salasnich 1997a,b).

In figure 3 we show the tunneling amplitude A as a function of the mean energy $\bar{E}$. We compare the exact results with the semiclassical ones at 1st (Landau), 3rd and 5th order in $\hbar$. We observe that, as expected, there is a better agreement by increasing the energy because at high energy the classical momentum of the particle is large and thus the de Broglie wavelength sufficiently small for the semiclassical methods to be applicable. In figure 4 (5) we plot the tunneling amplitude A as a function $\hbar_{eff}$ for the first (fourth) pair of almost degenerate consecutive energy levels. As shown also in table 1, the semiclassical results approach the exact ones by increasing the perturbative order in $\hbar$. Note that at the 5th order in $\hbar$ the agreement with exact result is up to the 8th digit.

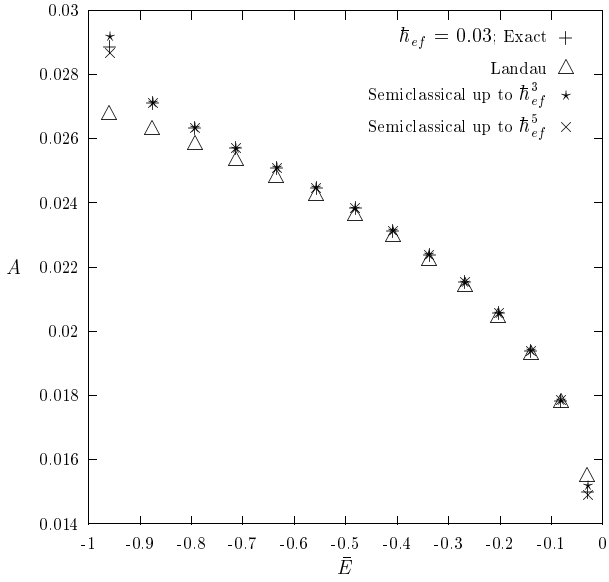

Figure 3: Tunneling amplitude A *vs* mean energy $\bar{E}$ of Quartic potential with $\hbar_{eff}=0.03$.

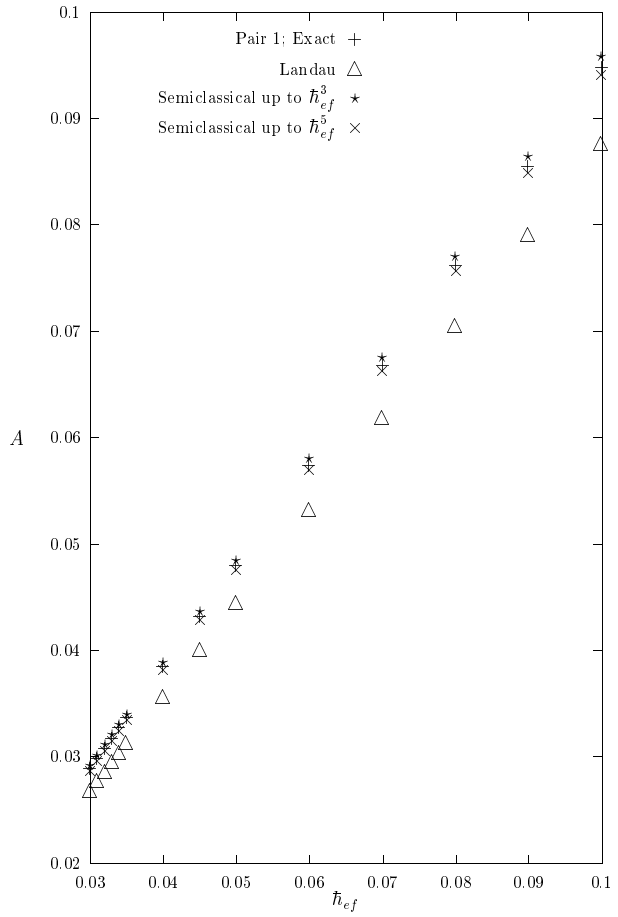

Figure 4: Tunneling amplitude A *vs* $\hbar_{eff}$ for the first pair of almost degenerate consecutive energy levels. Quartic potential.

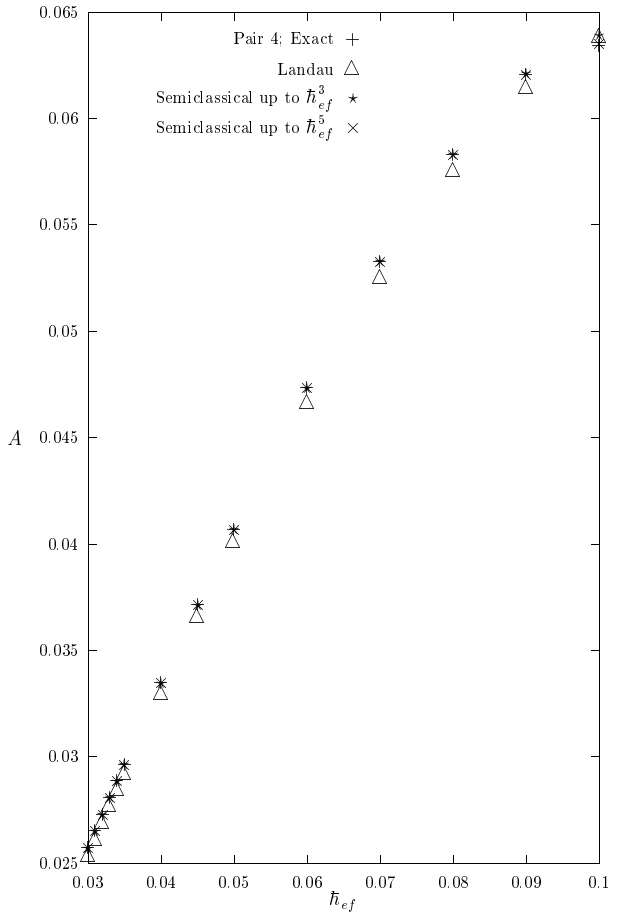

Figure 5: Tunneling amplitude A *vs* $\hbar_{eff}$ for the forth pair of almost degenerate consecutive energy levels. Quartic potential.

Table 1: Energy splitting $\Delta\bar{E}$ for almost degenerate pairs at $\hbar_{eff} = 0.03$. $\bar{E}_s$ is the exact mean energy, $\Delta\bar{E}_{Landau}$, $\Delta\bar{E}_{\hbar^3}$ and $\Delta\bar{E}_{\hbar^5}$ are the semiclassical results at 1st (Landau), 3rd and 5th order, respectively. In the last column of the upper table: exact energy splitting in units of mean level spacing.

Pair number	$\bar{E}_s$	$\Delta\bar{E}_{Exact}$	$\Delta\bar{E}_n/(\overline{\bar{E}_s^{n+1} - \bar{E}_s^n})$
1	-0.9578013510838623	9.232(2)E-28	1.291(6)E-26
2	-0.8743363182686136	6.533698E-25	9.140541E-24
3	-0.7923227236203907	2.197647599E-22	3.074474586E-21
4	-0.7118393444104010	4.66709587543E-20	6.52919406381E-19
5	-0.6329771419061873	7.0097983270055E-18	9.8065981172742E-17
6	-0.5558426330893027	7.901944841994295E-16	1.10546971247045E-14
7	-0.4805627052945287	6.920784581323967E-14	9.68206928062435E-13
8	-0.4072917698084478	4.806630946488390E-12	6.72440144371474E-11
9	-0.3362229365299848	2.675674688376366E-10	3.74322699989559E-09
10	-0.2676066496781732	1.196767019706533E-08	1.67425832453064E-07
11	-0.2017846855780184	4.273586943459416E-07	5.97868122857108E-06
12	-0.1392610433553887	1.195177462312803E-05	1.67203455862220E-04
13	-8.088844930248588E-02	2.500127371158503E-04	3.49763905139656E-03
14	-2.855578436131249E-02	3.352190557610379E-03	4.68966210972998E-02

$\Delta\bar{E}_{Landau}(\bar{E}_s)$	$\Delta\bar{E}_{\hbar^3}(\bar{E}_s)$	$\Delta\bar{E}_{\hbar^5}(\bar{E}_s)$
8.56386072023299E-28	9.**3**3424576483334E-28	9.1**6**991849898935E-28
6.**3**4511775769322E-25	6.53**7**96204696428E-25	6.533**3**2080224002E-25
2.1**5**758453279967E-22	2.197**9**8578660872E-22	2.1976**3**766003663E-22
4.6**0**423712282166E-20	4.667**3**7049838592E-20	4.66709**2**38092202E-20
6.9**3**436277656352E-18	7.010**0**0176474235E-18	7.00979**7**08264343E-18
7.8**3**077639810467E-16	7.902**0**7840692513E-16	7.901944**5**833250E-16
6.8**6**703907509728E-14	6.9208**6**233123417E-14	6.920784**5**1430764E-14
4.7**7**381431395796E-12	4.8066**7**193943203E-12	4.806630**8**878842E-12
2.6**5**943820818162E-10	2.6756**9**528644699E-10	2.675674**7**543535E-10
1.19**0**31027734624E-08	1.1967**7**788146677E-08	1.196767**1**4995564E-08
4.2**5**353592752249E-07	4.2736**5**612082292E-07	4.27358**9**20983707E-07
1.19**0**79278916304E-05	1.1952**4**083756918E-05	1.19518**3**71126262E-05
2.49**8**35207740361E-04	2.50**1**42635772383E-04	2.500**5**8564705645E-04
3.**4**6270869995442E-03	3.3**9**489990444765E-03	3.3**3**278741702504E-03

7 Conclusions

In this work we have taken the first step towards a systematic improvement of the Landau formula (Landau and Lifshitz 1997), which is the semiclassical leading order energy level splitting formula for pairs of almost degenerate levels in double well potentials. We have developed the algorithm for the semiclassical $\hbar$ expansion series to all orders for the tunneling amplitude A (of equation (1)), and thus calculated explicitly the quantum corrections up to the 5th order. We have compared the semiclassical predictions with the exact results obtained numerically, in quadruple precision in case of the quartic double well potential. Our approach is based on the usual WKB expansion in one–dimensional potentials. Thus the calculation of higher corrections can in principle be continued by the same method, although the structure of higher terms increases in complexity very quickly. We have also shown what happens in cases where the assumption implicit in the Landau formula (namely the linearity of the potential around the turning points) is not satisfied: We get a different result even in the leading semiclassical order, and this has been shown for the double square well potential. We should stress that the Landau formula (1997) is indeed quite good approximation since it always yields the correct order of magnitude (the exponential tunneling factor is always exact) and even the tunneling amplitude is correct within the 5–50 % .

It is our goal to work out a more direct WKB approach to the solution of the multi–minima problem, by the contour integration technique, based on requiring the single valuedness of the eigenfunction, as has been done in the case of a single well potential in (Robnik and Salasnich 1997a,b). This is our future project.

Finally we should mention important applications e.g. in the domain of molecular physics (Herzberg 1991, Landau and Lifshitz 1997, Cohen-Tannoudji *et al* 1993). For example, the NH_3 molecule can be described by a quasi one-dimensional potential $V(x)$ as a function of the perpendicular distance x of the nitrogen N atom from the H_3 plane, and as such it has the double well form, with the top of the potential barrier at $x = 0$. In order to calculate the energy level splitting of the doublets of vibrational modes one needs exactly our theory. Another example is the torsional motion of C_2H_4 molecule, where again we encounter an effectively one-dimensional double well potential. In case of C_2H_6 molecule, we find three potential wells where the tunneling effects again determine the splittings of energy triplet levels and a generalization of our theory would give an improved estimate of the splittings.

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Appendix

The semiclassical splitting formula is obtained by inserting the semiclassical wavefunction $\psi_0(x)$ for the classically forbidden region $|x| < a$

$$\psi_0(x) = \frac{C}{\sqrt{|\tilde{p}|}} \exp\left[\frac{1}{\hbar}\left(\int_a^x |\tilde{p}|\, dx + \tilde{\sigma}_{even} + \tilde{\sigma}_{odd}\right)\right] ;$$

$$\tilde{\sigma}_{even} = \sum_{k=1}^{\infty} \hbar^{2k} \tilde{\sigma}_{2k} \,, \tag{59}$$

$$\tilde{\sigma}_{2k}(x) = \int_a^x \tilde{\sigma}'_{2k}(|\tilde{p}(\xi)|) d\,\xi \,,$$

$$\tilde{\sigma}_{odd} = \sum_{k=1}^{\infty} \hbar^{2k+1} \tilde{\sigma}_{2k+1} \,,$$

$$\tilde{\sigma}_{2k+1}(x) = \int^x \tilde{\sigma}'_k(|\tilde{p}(\xi)|) d\,\xi \,,$$

into the general expression (8). The potential $V(x)$ can always be written in the way where the maximum of the barrier is at the point $x = 0$. Considering that, and inserting (59) into (8) we

get

$$\Delta E = \frac{2\hbar C^2}{m|\tilde{p}|}(|\tilde{p}| + \tilde{\sigma}'_{even} + \tilde{\sigma}'_{odd}) \times \exp\left[\frac{2}{\hbar}\left(\int_a^0 |\tilde{p}|\, dp + \tilde{\sigma}_{even} + \tilde{\sigma}_{odd}\right)\right]. \quad (60)$$

The exponent of all terms except the leading one can be expanded in the $\hbar$ power series. The expression valid up to the 5th order in $\hbar$ expansion reads as

$$\begin{aligned}\Delta E = \frac{2\hbar C^2}{m}\Bigg[& 1 + \hbar 2\tilde{\sigma}_2(0) \\ & + \hbar^2\left(\frac{\tilde{\sigma}'_2(0)}{\tilde{\sigma}'_0(0)} + 2\tilde{\sigma}_2^2(0) + 2\tilde{\sigma}_3(0)\right) \\ & + \hbar^3\left(2\tilde{\sigma}_4(0) + \frac{4}{3}\tilde{\sigma}_2^3(0) + 4\tilde{\sigma}_2(0)\tilde{\sigma}_3(0)\right) \\ & + \hbar^3\left(\frac{\tilde{\sigma}'_3(0)}{\tilde{\sigma}'_0(0)} + 2\tilde{\sigma}_2\frac{\tilde{\sigma}'_2(0)}{\tilde{\sigma}'_0(0)}\right) \\ & + \hbar^4\left(\frac{\tilde{\sigma}'_4(0)}{\tilde{\sigma}'_0(0)} + 2\frac{\tilde{\sigma}'_2(0)}{\tilde{\sigma}'_0(0)}\left(\tilde{\sigma}_2^2(0) + \tilde{\sigma}_3(0)\right)\right) \\ & + \hbar^4\left(2\tilde{\sigma}_2(0)\frac{\tilde{\sigma}'_3(0)}{\tilde{\sigma}'_0(0)} + 2\tilde{\sigma}_5(0) + \frac{2}{3}\tilde{\sigma}_2^4(0)\right) \\ & + \hbar^4\left(2\tilde{\sigma}_3^2(0) + 4\tilde{\sigma}_2(0)\tilde{\sigma}_4(0) + 4\tilde{\sigma}_2^2(0)\tilde{\sigma}_3(0)\right)\Bigg] \\ & \times \exp\left[-\frac{2}{\hbar}\int_0^a |\tilde{p}|\, dx\right].\end{aligned}$$

Using the recursive relation for $\tilde{\sigma}'_k$ we observe that certain combinations in the tunneling amplitude in the upper equation are the integrals of functions identical to 0, evaluated in $x = 0$. In the term that stands with $\hbar^2$ such a combination is

$$\frac{d}{dx}\left(\frac{\tilde{\sigma}'_2(x)}{\tilde{\sigma}'_0(x)} + 2\tilde{\sigma}_3(x)\right) = = \frac{2\tilde{\sigma}'_3(x)\tilde{\sigma}'_0(x) + 2\tilde{\sigma}'_2(x)\tilde{\sigma}'_1(x) + \tilde{\sigma}''_2(x)}{\tilde{\sigma}'_0(x)} = 0\,. \quad (61)$$

The same combination multiplied by $\tilde{\sigma}_2$ and $\tilde{\sigma}_2^2$ can be also found in the brackets after $\hbar^3$ and $\hbar^4$. In the bracket after $\hbar^4$ one more combination like that can be found

$$\begin{aligned}\frac{d}{dx}\left(2\tilde{\sigma}_5(x) + 2\tilde{\sigma}_3^2(x) + \frac{\tilde{\sigma}'_4(x)}{\tilde{\sigma}'_0(x)} + 2\tilde{\sigma}_3(x)\frac{\tilde{\sigma}'_2(x)}{\tilde{\sigma}'_0(x)}\right) = \\ = \Bigg(\frac{2\tilde{\sigma}'_5(x)\tilde{\sigma}'_0(x) + 2\tilde{\sigma}'_4(x)\tilde{\sigma}'_1(x)}{\tilde{\sigma}'_0(x)} \\ + \frac{2\tilde{\sigma}'_3(x)\tilde{\sigma}'_2(x) + \tilde{\sigma}''_4(x)}{\tilde{\sigma}'_0(x)}\Bigg) \\ + 2\tilde{\sigma}_3(x)\frac{2\tilde{\sigma}'_3(x)\tilde{\sigma}'_0(x) + 2\tilde{\sigma}'_2(x)\tilde{\sigma}'_1(x) + \tilde{\sigma}''_2(x)}{\tilde{\sigma}'_0(x)} \\ = 0\,.\end{aligned} \quad (62)$$

In this way the simplified splitting formula valid up to the 5th order expansion is found

$$\begin{aligned}\Delta E = \frac{2\hbar C^2}{m}\Bigg[& 1 + \hbar 2\tilde{\sigma}_2(0) + \hbar^2 2\tilde{\sigma}_2^2(0) \\ & + \hbar^3\left(2\tilde{\sigma}_4(0) + \frac{4}{3}\tilde{\sigma}_2^3(0) + \frac{\tilde{\sigma}'_3(0)}{\tilde{\sigma}'_0(0)}\right) \\ & + \hbar^4\left(2\tilde{\sigma}_2(0)\frac{\tilde{\sigma}'_3(0)}{\tilde{\sigma}'_0(0)}\right) \\ & + \hbar^4\left(\frac{2}{3}\tilde{\sigma}_2^4(0) + 4\tilde{\sigma}_2(0)\tilde{\sigma}_4(0)\right)\Bigg] \\ & \times \exp\left[-\frac{2}{\hbar}\int_0^a |\tilde{p}|\, dx\right]\end{aligned} \quad (63)$$

and by taking into account the even symmetry of the potential $V(x)$ due to which the first derivatives of all odd $\tilde{\sigma}_k$ evaluated at $x = 0$ are zero, we obtain equation (24).

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