On a semiclassical formula for non-diagonal matrix elements

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Abstract

Let $H(\hbar) = -\hbar^2 d^2/dx^2 + V(x)$ be a Schrödinger operator on the real line, $W(x)$ be a bounded observable depending only on the coordinate and k be a fixed integer. Suppose that an energy level E intersects the potential $V(x)$ in exactly two turning points and lies below $V_\infty = \liminf_{|x|\to\infty} V(x)$. We consider the semiclassical limit $n \to \infty$, $\hbar = \hbar_n \to 0$ and $E_n = E$ where E_n is the nth eigen-energy of $H(\hbar)$. An asymptotic formula for $\langle n|W(x)|n+k\rangle$, the non-diagonal matrix elements of $W(x)$ in the eigenbasis of $H(\hbar)$, has been known in the theoretical physics for a long time. Here it is proved in a mathematically rigorous manner.

Keywords: semiclassical limit, non-diagonal matrix elements, WKB method

1 Introduction

In the quantum mechanics the matrix elements of an observable occur in various situations. Let us mention few of them. They measure transition probabilities between two states and the coefficients in the stationary perturbation theory are expressed in terms of the matrix elements of the perturbation. The distribution of matrix elements is of interest for quantum systems stemming from classically chaotic systems, see for example [9, 6] and references in the latter paper. Our immediate motivation to study the matrix elements was the quantum version of the Kolmogorov-Arnold-Moser method [1], [8]. One of the assumptions under which this method is applicable is that a time-dependent perturbation of a quantum system must be sufficiently small with respect to certain norm which is also expressed in terms of matrix elements.

One may hope to obtain at least a qualitative information about the behavior of matrix elements when considering the semiclassical limit. In fact this idea goes back to the very origins of the quantum mechanics. A semiclassical formula for non-diagonal matrix elements in the one-dimensional case has been suggested already a long time ago [12]. In [9] one can find another derivation, also on the level of rigor usual in the theoretical physics, for absolute values of the non-diagonal matrix elements.

Despite of the ancient history rigorous mathematical results have been published essentially more recently. Moreover, they cover only some particular cases even though the technical tools necessary for the derivation may be at hand nowadays. One usually assumes that the corresponding classical system is either ergodic [5], [6] or completely integrable [19], [2], [15], [7]. The semiclassical limit of diagonal matrix elements is now treated in detail [5]. In the case of multi-dimensional completely integrable systems a formula for non-diagonal matrix elements was proved in [19], [15], [7], see also [16] for some generalizations. The one-dimensional case seems to be rather particular. In [14] one can find a derivation of the semiclassical formula for pseudo-differential operators in one variable such that the Weyl symbol of the Hamiltonian is a real polynomial on the phase space while imposing an additional assumption on the discreteness of the operator spectrum.

The present paper aims to provide a mathematically rigorous verification of the semiclassical limit of non-diagonal matrix elements for Schrödinger operators on the real line. We prove the formula under mild assumptions on the potential. In addition, we take care about identifying the quantum number coming from the Bohr-Sommerfeld quantization condition with the index determined by the natural enumeration of eigenvalues in ascending order. Our approach relies on a transparent application of some well established tools in the spectral and semiclassical analysis. So we briefly recall the corresponding results while adjusting their formulation to our purposes. On the other hand, the chosen method restrict us to considering observables which depend on the coordinate only. This particular case was sufficient for the applications we originally had in mind, as mentioned above.

Let us now formulate precisely in what sense the semiclassical limit is understood. Set

$$H(\hbar) = -\hbar^2 \frac{d^2}{dx^2} + V(x) \quad \text{in } L^2(\mathbb{R}, dx). \tag{1}$$

We consider a fixed energy E and an observable $W = W(x)$ depending only on the coordinate x. The assumptions are as follows.

We suppose that $V(x)$ is bounded from below and three times continuously differentiable, $W(x)$ is bounded and continuously differentiable,

$$E < V_\infty := \liminf_{|x|\to\infty} V(x). \tag{2}$$

We assume that at the energy E there are exactly two regular turning points, i.e., $V^{-1}(E) = \{x_-, x_+\}$, $x_- < x_+$, and $V'(x_\pm) \neq 0$. Set

$$f(x) = V(x) - E. \tag{3}$$

In addition we introduce an assumption making it possible to apply the WKB approximation, namely we assume that

$$\int_{\mathbb{R}\setminus[-a,a]} \left| \frac{1}{f^{1/4}} \frac{\mathrm{d}^2}{\mathrm{d}x^2} \left(\frac{1}{f^{1/4}} \right) \right| \mathrm{d}x < \infty \tag{4}$$

where a is a positive number chosen so that $f(x) \geq \delta > 0$ for $|x| \geq a$. Notice that

$$\frac{1}{f^{1/4}} \frac{\mathrm{d}^2}{\mathrm{d}x^2} \left(\frac{1}{f^{1/4}} \right) = \frac{5(V')^2 - 4(V-E)V''}{16(V-E)^{5/2}} \,.$$

It may be convenient to replace condition (4) by two simpler conditions,

$$\int_{\mathbb{R} \setminus [-a,a]} \frac{|V'|^2}{(V-E)^{5/2}} \, \mathrm{d}x < \infty, \quad \int_{\mathbb{R} \setminus [-a,a]} \frac{|V''|}{(V-E)^{3/2}} \, \mathrm{d}x < \infty. \tag{5}$$

The part of the spectrum of $H(\hbar)$ lying below V_∞ is known to be formed exclusively of simple isolated eigenvalues. We fix the phase of an eigenfunction ψ_n corresponding to an eigenvalue $E_n < V_\infty$ by requiring ψ_n to be positive on a neighborhood of $+\infty$. Moreover, there exists a strictly decreasing sequence of positive numbers tending to 0, $\{\hbar_n\}_{n=n_0}^{\infty}$, and a constant $\hbar_0 > 0$ such that for $\hbar \in]0, \hbar_0]$, E belongs to the spectrum of $H(\hbar)$ if and only if $\hbar = \hbar_n$ and in that case $E = E_n$ is the nth eigenvalue of $H(\hbar)$ provided the enumeration of eigenvalues starts from the index $n = 0$.

Under these assumptions we claim that if $k \in \mathbb{Z}$ is fixed, $n \to \infty$, $\hbar = \hbar_n \to 0$, with $E = E_n$, then

$$\langle n | W(x) | n+k \rangle \to \frac{1}{T} \int_0^T W(q(t))\, e^{ik\omega t} \, \mathrm{d}t \tag{6}$$

where $(q(t), p(t))$, $t \in [0, T]$, is the classical trajectory in the phase space at the energy E and with the initial point chosen so that the kinetic energy vanishes, i.e., $p(0) = 0$, and $q(0)$ coincides the right turning point x_+. Furthermore, $T > 0$ is the period of the classical motion and $\omega = 2\pi/T$ is the frequency.

Remark. If the phase of the wave function ψ_n was chosen so that ψ_n was positive on a neighborhood of $-\infty$ then formula (6) would be again true with $(q(0), p(0)) = (x_-, 0)$.

As already said, we have confined ourselves to observables depending only on the coordinate because our method of proof is based on the WKB approximation. One naturally expects, however, that for any smooth bounded classical observable $A(q, p)$,

$$\langle n | \hat{A} | n+k \rangle \to \frac{1}{T} \int_0^T A(q(t), p(t))\, e^{ik\omega t} \mathrm{d}t$$

where $\hat{A}$ is a suitable quantization of A. We have already mentioned that this result is actually proved in [14] in the case when the potential $V(x)$ is a polynomial.

Let us rewrite the RHS in formula (6). The equation of the classical trajectory in the phase space reads $p^2 + V(x) = E$ and its period equals

$$T = \int_{x_-}^{x_+} \frac{\mathrm{d}x}{\sqrt{E - V(x)}} \,. \tag{7}$$

For $x \in [x_-, x_+]$ set

$$\tau(x) = \frac{1}{2} \int_x^{x_+} \frac{\mathrm{d}y}{\sqrt{E - V(y)}} \,. \tag{8}$$

Then $\tau(x_+) = 0$, $\tau(x_-) = T/2$, $q(\tau(x)) = x$, and

$$\int_0^T W(q(t))\, e^{ik\omega t}\, \mathrm{d}t = \int_{x_-}^{x_+} \frac{W(x)}{\sqrt{E - V(x)}} \cos\!\left(\frac{2\pi k}{T}\, \tau(x)\right) \mathrm{d}x.$$

The paper is organized as follows. In Sections 2 through 4 we recall some preliminaries that we need for the proof of the formula. Section 2 is devoted to the basic spectral properties of the Schrödinger operator, Section 3 is concerned with the Weyl asymptotic formula and some basic facts about the WKB approximation are summarized in Section 4. By counting the zeroes of wave functions we show in Section 5 that the quantum number coming from the Bohr-Sommerfeld quantization condition equals the index of the corresponding eigenvalue. The semiclassical formula is then proved in Section 6.

2 Properties of the spectrum lying below V_∞

Here we briefly recall two well known properties of Schrödinger operators. In the monographs they are usually formulated and derived for potentials diverging at infinity. We just wish to point up that the same assertions apply also for more general potentials provided one takes care only about the part of the spectrum lying below V_∞. The corresponding proofs can be taken almost literally from the cited monographs.

In this section (and only in it) the Planck constant is not relevant and so we set it equal to 1 and consider the Hamiltonian

$$H = -\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x) \quad \text{in } L^2(\mathbb{R}, \mathrm{d}x).$$

The following theorem is in fact widely used. We recall it in a form which is a direct modification of Theorem XIII.16 in [17]. Its proof is based on the min-max principle and is applicable in any dimension of the underlying Euclidean space. Moreover, the differentiability of $V(x)$ is not required.

Theorem 1. *Let V be a measurable function in $\mathbb{R}^n$ which is bounded from below. Define $H = -\Delta + V$ as the sum of quadratic forms in $L^2(\mathbb{R}^n, \mathrm{d}^n x)$. Then the lower edge of the essential spectrum of H, if any, is greater than or equal to $V_\infty = \liminf_{|x|\to\infty} V(x)$.*

Let us note that in the one-dimensional case and provided the potential is continuous Theorem 1 also follows from a well known estimate on the number of negative eigenvalues.

Here and everywhere in what follows, if A is a self-adjoint operator then $P(A; \cdot)$ designates the associated projector-valued measure, and for $K \in \mathbb{R}$ we denote

$$N(A, K) = \operatorname{rank} P(A;]-\infty, K[).$$

Further, for a real-valued function $W(x)$ we set

$$W_-(x) = \max\{0, -W(x)\}.$$

It holds (see, for example, Theorem 5.3 in [3])

$$N(H,0) \le 1 + \int_{\mathbb{R}} |x|\, V_-(x)\,\mathrm{d}x.$$

In particular, if $V(x)$ is continuous and bounded from below then for any $c < V_\infty$ the function $(V-c)_-(x)$ has a compact support and, by this estimate, $N(H,c) < \infty$. This again implies that the lower edge of the essential spectrum of H is greater than or equal to V_∞.

The next property is specific for the one-dimensional case. The potential $V(x)$ is supposed to be continuous and bounded from below.

As is well known from the theory of ordinary differential equations, for $E < V_\infty$, any nontrivial solution of the Schrödinger equation either grows at least exponentially or decays at least exponentially at $+\infty$ (see, for example, Corollary 1 in [3, Section II]). The latter solution is called recessive at $+\infty$ and is unique up to a multiplicative constant. Of course, an analogous assertion is also true for $-\infty$. It immediately follows that all eigenvalues of the Hamiltonian H lying below V_∞ are simple. Moreover, in virtue of Theorem 1, they have no accumulation points below V_∞. Consequently, the eigenvalues of H below V_∞ can be arranged into a strictly increasing sequence, empty or finite or infinite,

$$E_0 < E_1 < E_2 < \ldots < V_\infty.$$

The following theorem is a straightforward modification of Theorem 3.5 in [3, Chapter II].

Theorem 2. *The number of zeroes of the mth eigenfunction of H corresponding to the eigenvalue $E_m < V_\infty$ is exactly equal to m.*

3 The Weyl asymptotic formula

In this section we aim to recall the Weyl asymptotic formula generalized to Schrödinger operators. It can be derived from the Gutzwiller trace formula [10] which was rigorously proved in [4] under the assumption that the potential is positive and infinitely differentiable. In [18] there is given a short review of the history and the Weyl asymptotic formula is recalled even under stricter assumptions which among others mean that the potential does not grow faster than polynomially. A weaker version of the formula is also stated in [17, Theorem XIII.79] but only for compactly supported potentials.

Here we wish to point out that the proof of Theorem XIII.79 in [17] can be extended in a straightforward manner and thus the Weyl asymptotic formula can be derived just under the assumption that the potential is semi-bounded and continuous. We restrict ourselves, however, to the one-dimensional case only. In addition, this approach is quite simple as it is based merely on an application of the min-max principle and the Dirichlet-Neumann bracketing. On the other hand, if compared to the result based on the trace formula, as presented in [18], the control of the error term is essentially worse;

it is known to be of order $O(1)$ while the present method only yields the asymptotic behavior of the type $o(\hbar^{-1})$.

From now on, the Planck constant is again relevant. This means that the discussion concerns the Hamiltonian $H(\hbar)$ introduced in (1). Since what follows is nothing but a slight modification of known results we just indicate the basic steps.

First let us recall a definition from [17, XIII.15] making it possible to compare self-adjoint operators defined in different Hilbert spaces. The symbol $Q(A)$ stands for the form domain of A. If $\psi \in Q(A)$ then the scalar product $\langle \psi, A\psi \rangle$ is automatically understood in the form sense.

Definition. Let $\mathcal{H}_1 \subset \mathcal{H}$ be a closed subspace, let A be a semi-bounded self-adjoint operator in $\mathcal{H}$ and let B be a semi-bounded self-adjoint operator in $\mathcal{H}_1$. We shall write $A \leq B$ if and only if it holds

(i) $Q(A) \supset Q(B)$,

(ii) $\forall \psi \in Q(B)$, $\langle \psi, A\psi \rangle \leq \langle \psi, B\psi \rangle$.

With the aid of the min-max principle one can show [17, XIII.15] that if $A \leq B$ then

(i) $\forall K \in \mathbb{R}$, $\operatorname{rank} P(A;]-\infty, K[) \geq \operatorname{rank} P(B;]-\infty, K[)$,

(ii) $\forall K \in \mathbb{R}$, $\operatorname{rank} P(A;]-\infty, K]) \geq \operatorname{rank} P(B;]-\infty, K])$.

The following lemma is analogous to Proposition 2 in [17, XIII.15] in the one-dimensional case and its proof is based on rather elementary explicit computations of the eigenvalues for the involved operators.

Lemma 1. *Let $I = [a, b]$ be a compact interval. Let us introduce H_D, H_N and H_M as self-adjoint operators in $L^2(I, \mathrm{d}x)$ such that all of them act as the differential operator $-\hbar^2\, \mathrm{d}^2/\mathrm{d}x^2$ and whose domain is respectively determined by the Dirichlet, Neumann and mixed boundary conditions. Then for all $K > 0$ it holds*

$$-1 \leq \operatorname{rank} P(H;]-\infty, K[) - \frac{\ell}{\pi\hbar}\sqrt{K} \leq \operatorname{rank} P(H;]-\infty, K]) - \frac{\ell}{\pi\hbar}\sqrt{K} \leq 1,$$

where H is any of the operators H_D, H_N, H_M, and $\ell = b - a$ is the length of the interval.

The following lemma coincides with Proposition 4 in [17, XIII.15] in the one-dimensional case.

Lemma 2. *Let $-\infty < a < b < c < +\infty$ and let H be a self-adjoint operator in $L^2([a, c], \mathrm{d}x)$ which acts as the differential operator $-\mathrm{d}^2/\mathrm{d}x^2$ with either the Dirichlet or the Neumann boundary condition imposed at each of the points a and c (mixed boundary conditions are admitted). Let $H_D^{(1)}$ and $H_N^{(1)}$ be the self-adjoint operators in $L^2([a, b], \mathrm{d}x)$ also acting as $-\mathrm{d}^2/\mathrm{d}x^2$ and with the domain being determined by the same boundary condition at the point a as imposed in the case of the operator H and by the*

Dirichlet or Neumann boundary condition at the point b*, respectively. Analogously one introduces the self-adjoint operators* $H_D^{(2)}$ *and* $H_N^{(2)}$ *in* $L^2([b,c],\mathrm{d}x)$*. Then it holds*

$$H_N^{(1)} \oplus H_N^{(2)} \leq H \leq H_D^{(1)} \oplus H_D^{(2)}.$$

First let us state the Weyl asymptotic formula for a finite interval. It can be prover in a way very close to the proof of Theorem XIII.79 in [17]. So we do not reproduce the proof but let us note that it is based on a limit procedure when the interval is split into N subintervals of equal length with N tending to ∞. In the course of the proof one uses Lemma 1 and 2, the additivity of the numbers $N(A,K)$, i.e.,

$$N(A_1 \oplus A_2 \oplus \ldots \oplus A_N, K) = N(A_1,K) + N(A_2,K) + \ldots + N(A_N,K),$$

and the fact that the integral on the RHS of (9) exists in the Riemann sense.

Theorem 3. *Let* $-\infty < a < b < +\infty$*,* $V \in C([a,b])$*, and let*

$$H_f(\hbar) = -\hbar^2 \frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x)$$

be a self-adjoint operator in $L^2([a,b],\mathrm{d}x)$ *with either the Dirichlet or Neumann boundary condition imposed at each of the boundary points* a *and* b *(mixed boundary conditions are admitted). Then for all* $K \in \mathbb{R}$*,*

$$\lim_{\hbar\to 0+} \hbar\, N(H_f(\hbar),K) = \frac{1}{\pi}\int_a^b \sqrt{(V-K)_-(x)}\,\mathrm{d}x. \tag{9}$$

Finally let us proceed to the case of the Hamiltonian $H(\hbar)$.

Theorem 4. *Let* $V \in C(\mathbb{R})$ *be a real-valued function which is bounded from below. Then for all* $K < V_\infty$ *it holds true that*

$$\lim_{\hbar\to 0+} \hbar\, N(H(\hbar),K) = \frac{1}{2\pi}\mathrm{Vol}_Z\left(\mathscr{H}^{-1}(]-\infty,K[)\right) = \frac{1}{\pi}\int_{\mathbb{R}} \sqrt{(V-K)_-(x)}\,\mathrm{d}x \tag{10}$$

where $\mathscr{H}(x,p) = p^2 + V(x)$ *and* $\mathrm{Vol}_Z(X)$ *designates the Lebesgue measure of a measurable set* X *in the phase space.*

Proof. If $K < V_\infty$ then the support of $(V-K)_-$ is compact. Suppose that $\mathrm{supp}(V-K)_- \subset [a,b]$, $-\infty < a < b < +\infty$. Set

$$H_1(\hbar) = -\hbar^2 \frac{\mathrm{d}^2}{\mathrm{d}x^2} - (V-K)_-(x) \quad \text{in } L^2(\mathbb{R},\mathrm{d}x)$$

and

$$H_2(\hbar) = -\hbar^2 \frac{\mathrm{d}^2}{\mathrm{d}x^2} + V(x) - K \quad \text{in } L^2([a,b],\mathrm{d}x)$$

with the Dirichlet boundary condition imposed at the points a and b. Observe that $-(V-K)_-(x) \leq V(x) - K$ on $\mathbb{R}$ and so $Q(H(\hbar)-K) \subset Q(H_1(\hbar))$. Furthermore,

$L^2([a,b],\mathrm{d}x)$ can be naturally regarded as a subspace in $L^2(\mathbb{R},\mathrm{d}x)$. If $\psi \in Q(H_2(\hbar))$ then $\tilde{\psi}$ defined by $\tilde{\psi}(x)=\psi(x)$ for $x\in[a,b]$, $\tilde{\psi}(x)=0$ for $x\in\mathbb{R}\setminus[a,b]$, belongs to $Q(H(\hbar)-K)$ ($\tilde{\psi}$ is an absolutely continuous function). This implies that $Q(H_2(\hbar))\subset Q(H(\hbar)-K)$. We have find that $H_1(\hbar)\le H(\hbar)-K\le H_2(\hbar)$. Hence

$$N(H_2(\hbar),0)\le N(H(\hbar),K)\le N(H_1(\hbar),0).$$

Formula (10) for compactly supported potentials is stated in [17, Theorem XIII.79]. Hence it holds

$$\lim_{\hbar\to 0+}\hbar\, N(H_1(\hbar),0)=\frac{1}{\pi}\int_{\mathbb{R}}\sqrt{(V-K)_-(x)}\,\mathrm{d}x,$$

and from Theorem 3 we know that

$$\lim_{\hbar\to 0+}\hbar\, N(H_2(\hbar),0)=\frac{1}{\pi}\int_a^b\sqrt{(V-K)_-(x)}\,\mathrm{d}x=\frac{1}{\pi}\int_{\mathbb{R}}\sqrt{(V-K)_-(x)}\,\mathrm{d}x.$$

Formula (10) for a general potential then follows by bracketing. □

For our purposes the following immediate corollary of Theorem 4 will be sufficient. Suppose that $V(x)$ is continuously differentiable and an interval $]a,b[$, $a<b\le V_\infty$, contains at least one regular value of the classical Hamiltonian $\mathscr{H}(x,p)$, i.e., there exists $\lambda\in]a,b[$ satisfying $\mathscr{H}^{-1}(\{\lambda\})\neq\emptyset$ and $V(x)=\lambda$ implies $V'(x)\neq 0$. Then the number of eigenvalues of $H(\hbar)$ in the interval $]a,b[$ tends to infinity as $\hbar\to 0+$.

4 The WKB method for one and two turning points

Here we summarize some basic facts about the WKB approximation, also called Liouville-Green approximation, that we need for the proof of the formula in Section 6. At the same time we introduce the necessary notation. We stick to the presentation given in the monograph [13] whose distinguished feature is that it provides explicit bounds on the error terms.

Let us first consider the situation with one turning point. Let $]a,b[\subset\mathbb{R}$ be an interval, finite or infinite, $x_0\in]a,b[$, and $f(x)$ be a real-valued function defined on $]a,b[$ such that $f(x)/(x-x_0)$ is positive and twice continuously differentiable (hence $f(x_0)=0$, $f'(x_0)>0$). For $x\in]a,b[$ set

$$\frac{2}{3}\,\zeta^{3/2}=\int_{x_0}^{x}\sqrt{f(t)}\,\mathrm{d}t\qquad\text{if } x\ge x_0,\tag{11a}$$

$$\frac{2}{3}\,(-\zeta)^{3/2}=\int_{x}^{x_0}\sqrt{-f(t)}\,\mathrm{d}t\quad\text{if } x<x_0.\tag{11b}$$

Then $\zeta(x)$ is strictly monotone, $\zeta(x)/(x-x_0)$ is positive and twice continuously differentiable in $]a,b[$, see Lemma 3.1 in [13, Chapter 11].

Assume further that

$$\int_{x_0}^{b}\sqrt{f(t)}\,\mathrm{d}t=\infty\tag{12}$$

and

$$\int_{]a,b[\setminus U_0} \frac{|f''|}{|f|^{3/2}}\,\mathrm{d}t < \infty, \quad \int_{]a,b[\setminus U_0} \frac{(f')^2}{|f|^{5/2}}\,\mathrm{d}t < \infty, \tag{13}$$

where $U_0 = [x_0 - \varepsilon, x_0 + \varepsilon]$ and ε is any positive number such that $a < x_0 - \varepsilon$ and $x_0 + \varepsilon < b$.

Notice also that

$$\zeta' = \left(\frac{f}{\zeta}\right)^{1/2} \text{ and } \zeta'(x_0) = f'(x_0)^{1/3}. \tag{14}$$

Denote by ξ the inverse function to ζ. Theorem 3.1 in [13, Chapter 11, §3.3] can be rephrased as follows.

Theorem 5. *Under the above assumptions, the solution of the differential equation*

$$\hbar^2\,\frac{\mathrm{d}^2 w}{\mathrm{d}x^2} = f(x)w \tag{15}$$

which is recessive as x tends to b exists on $]a,b[$, is unique up to a multiplicative constant and equals

$$\psi(x) = \left(\frac{\zeta}{f}\right)^{1/4} \left(\mathrm{Ai}(\hbar^{-2/3}\zeta) + \varepsilon(\hbar, x)\right) \tag{16}$$

with the error term satisfying the estimates

$$|\varepsilon(\hbar,x)| \le \Phi_0(\hbar^{-2/3}\zeta)\,\hbar, \quad \left|\frac{\partial\varepsilon(\hbar,x)}{\partial x}\right| \le \left(\frac{f}{\zeta}\right)^{1/2} \Phi_1(\hbar^{-2/3}\zeta)\,\hbar^{1/3},$$

where $\Phi_0(x)$, $\Phi_1(x)$ are certain continuous positive functions on $\mathbb{R}$ such that

$$\Phi_0(x) \sim \begin{cases} \text{const}\,\dfrac{\exp\left(-\frac{2}{3}x^{3/2}\right)}{x^{1/4}} & \textit{as } x \to +\infty, \\[2ex] \text{const}\,\dfrac{1}{|x|^{1/4}} & \textit{as } x \to -\infty, \end{cases}$$

$$\Phi_1(x) \sim \begin{cases} \text{const}\,\exp\left(-\dfrac{2}{3}x^{3/2}\right) & \textit{as } x \to +\infty, \\[2ex] \text{const} & \textit{as } x \to -\infty. \end{cases}$$

Let us now turn to the case when $f(x)$ is given by (3) and so is defined on the entire real line. From now on the potential V satisfies all assumptions as formulated in the Introduction. In particular, it follows that the function

$$\frac{V(x) - E}{(x - x_-)(x - x_+)} \text{ is positive on } \mathbb{R} \text{ and belongs to } C^2(\mathbb{R}). \tag{17}$$

Moreover, there exists an open neighborhood of E, $U_E =]E_-, E_+[$, $E_- < E < E_+$, such that these assumptions apply for any $\lambda \in \overline{U_E}$ as well.

For $\lambda \in U_E$ set

$$\gamma_\lambda = \mathscr{H}^{-1}(\{\lambda\})$$

where $\mathscr{H}(x,p) = p^2 + V(x)$. Thus γ_λ is a closed curve in the phase space and the energy takes on it the value λ. Let us further introduce the action integral,

$$J(\lambda) = \int_{\mathscr{H}(x,p)\leq\lambda} \mathrm{d}x\mathrm{d}p = \int_{\gamma_\lambda} p\,\mathrm{d}x = 2\int_{x_-(\lambda)}^{x_+(\lambda)} \sqrt{\lambda - V(x)}\,\mathrm{d}x \tag{18}$$

where $x_-(\lambda) < x_+(\lambda)$ are the turning points at the energy λ. Then

$$T(\lambda) = J'(\lambda) = \int_{x_-(\lambda)}^{x_+(\lambda)} \frac{\mathrm{d}x}{\sqrt{\lambda - V(x)}} \tag{19}$$

is the period of the classical trajectory in the phase space.

In the following theorem we summarize the result derived in [13, Chapter 13, §8.2].

Theorem 6. *Under the assumptions on V formulated in the Introduction (in particular, we assume that condition (17) is fulfilled as well as the convergence of the integrals in (5)) there exist a neighborhood U_E of E, $\hbar_0 > 0$, $n_0 \in \mathbb{N}$ and for every $\lambda \in U_E$ a sequence $\{\hbar_n(\lambda)\}_{n=n_0}^\infty$, $\hbar_0 > \hbar_{n_0}(\lambda) > \hbar_{n_0+1}(\lambda) > \hbar_{n_0+2}(\lambda) > \ldots > 0$, such that for $\hbar \in]0, \hbar_0[$ the energy λ is an eigenvalue of $H(\hbar)$ if and only if $\hbar = \hbar_n(\lambda)$ for some $n \geq n_0$. Moreover, the sequence $\{\hbar_n(\lambda)\}$ asymptotically behaves like*

$$\hbar_n(\lambda)^{-1} = (2n+1)\pi J(\lambda)^{-1} + O(n^{-1}) \tag{20}$$

where the error term $O(n^{-1})$ decays in n uniformly with respect to $\lambda \in U_E$.

Remark. It is known that if $V \in C^r(\mathbb{R})$, with $r \geq 1$, and $E < V_\infty$ is a regular value of $V(x)$ then the action integral $J(\lambda)$ defined in (18) is r times continuously differentiable on some neighborhood of E (see, for example, [18]).

The verification of this assertion is quite elementary in the one-dimensional case and with two turning points at the energy E. For a sufficiently small neighborhood $U_E =]E_-, E_+[$ the function $V(x)$ is strictly decreasing on the interval $[x_-(E_+), x_-(E_-)]$ and strictly increasing on $[x_+(E_-), x_+(E_+)]$, with nowhere vanishing derivative. Let us write

$$\begin{aligned} T(\lambda) &= \left(\int_{x_-(\lambda)}^{x_-(E_-)} + \int_{x_-(E_-)}^{x_+(E_-)} + \int_{x_+(E_-)}^{x_+(\lambda)}\right) \frac{\mathrm{d}x}{\sqrt{\lambda - V(x)}} \\ &= T_-(\lambda) + T_0(\lambda) + T_+(\lambda). \end{aligned}$$

Clearly, $T_0(\lambda) \in C^\infty(U_E)$. Thus it is sufficient to verify that $T_-(\lambda), T_+(\lambda) \in C^{r-1}(U_E)$. Let us focus only on the latter function. Set $W_+ = \left(V\big|_{[x_+(E_-),x_+(E_+)]}\right)^{-1}$. Hence W_+

is r times continuously differentiable. After some elementary manipulations one can show that

$$T_+(\lambda) = \int_{x_+(E_-)}^{x_+(\lambda)} \frac{\mathrm{d}x}{\sqrt{\lambda - V(x)}} = 2\sqrt{\lambda - E_-} \int_0^1 \frac{\mathrm{d}t}{V'\big(W_+\big(\lambda(1-t^2) + E_- t^2\big)\big)} \,.$$

From the last expression it is obvious that $T_+(\lambda)$ is $r-1$ times continuously differentiable.

5 Number of zeroes derived from the WKB method

We need to show that if $\hbar = \hbar_m(\lambda)$ and hence λ is an eigenvalue of $H(\hbar)$, as claimed in Theorem 6, then λ is exactly the mth eigenvalue of $H(\hbar)$. According to Theorem 2, the index of an eigenvalue lying below V_∞ equals the number of zeroes of the corresponding eigenfunction. Fortunately, the WKB approximation, as explained in [13], is precise enough to control the number of zeroes.

Let us recall some facts concerning the Airy functions. Let us denote by a_n and b_n the zeroes of the Airy functions $\mathrm{Ai}(x)$ and $\mathrm{Bi}(x)$, respectively, arranged in ascending order of the absolute value, i.e., $\ldots < b_3 < a_2 < b_2 < a_1 < b_1 < 0$. It is known that

$$a_n = -\left(\frac{3}{2}\pi\left(n-\frac{1}{4}\right) + \mathfrak{z}\left(n-\frac{1}{4}\right)\right)^{2/3}, \quad b_n = -\left(\frac{3}{2}\pi\left(n-\frac{3}{4}\right) + \mathfrak{z}\left(n-\frac{3}{4}\right)\right)^{2/3}, \tag{21}$$

where $\mathfrak{z}(x) = O(x^{-1})$.

First we again consider the situation with one turning point. Recall defining relations (11a), (11b) for ζ. In the following theorem we summarize the results from §§ 6.1, 6.2 and 6.3 in [13, Chapter 11].

Theorem 7. *Under the same assumptions as in Theorem 5, let $w(x)$ be a nonzero solution of the differential equation (15) on $]a,b[$ which is recessive as x tends to b (hence $w(x)$ is unique up to a multiplicative constant). Then the set of zeroes of $w(x)$ in $]a,b[$, denoted $\{z_n\}_{n\geq 1}$ and arranged in descending order, is at most countable. Any such a zero z fulfills $\zeta(z) < \hbar^{2/3} b_1$. Furthermore, for all sufficiently small $\hbar$ it is true that if $\zeta(a) < \hbar^{2/3} b_{n+1}$ then the nth zero, z_n, does exist and obeys the estimate*

$$\hbar^{2/3} b_{n+1} < \zeta(z_n) < \hbar^{2/3} b_n.$$

Moreover, it holds

$$|\zeta(z_n) - \hbar^{2/3} a_n| = O(n^{-1/3})\hbar$$

where the symbol $O(n^{-1/3})$ is uniform with respect to $\hbar$.

Remarks. From Theorem 7 it immediately follows that there are no zeroes in the interval $[x_0, b[$. Furthermore, the number of zeroes of $w(x)$ in any fixed nonempty subinterval $]c,d[\, \subset\,]a, x_0[$ tends to infinity as $\hbar \to 0+$.

Now we come back to the case when $f(x)$ is given by (3), with $V(x)$ satisfying the assumptions from the Introduction. In particular, there are two turning points at the energy E, x_- and x_+, and $V(x)$ satisfies (17) and (5). Then for any a, $x_- < a < x_+$, the function $f(x)$ satisfies the assumptions of Theorem 7 with $b = +\infty$ and x_0 being replaced by x_+. Actually, condition (5) implies (13) and condition (12) is fulfilled automatically for $E < V_\infty$. Analogous arguments apply also for the other turning point x_-.

According to Theorem 6 there exist $\hbar_0 > 0$ and a sequence $\{\hbar_n\}_{n=n_0}^\infty$, $\hbar_0 > \hbar_{n_0} > \hbar_{n_0+1} > \hbar_{n_0+2} > \ldots > 0$, such that for $\hbar \in]0, \hbar_0[$, E is an eigenvalue of $H(\hbar)$ if and only $\hbar = \hbar_n$ for some $n \geq n_0$. Let $\psi_n(x)$ be an eigenfunction of $H(\hbar_n)$ corresponding to the eigenvalue E. Thus $\psi_n(x)$ is recessive both at $+\infty$ and $-\infty$ and is unique up to a multiplicative constant. We can suppose that $\hbar_0$ is sufficiently small so that $\psi_n(x)$ has at least one zero in the interval $]x_-, x_+[$. By Theorem 7, $\psi_n(x)$ has no zeroes in the set $\mathbb{R}\setminus]x_-, x_+[$.

Let us choose a point $x_1 \in]x_-, x_+[$ independently of n. Let x_1' be the zero of ψ_n which is nearest to x_1. This means that x_1' depends on n but the distance between x_1 and x_1' tends to zero as n tends to infinity. Denote by m_+ and m_- the number of zeroes of ψ_n in the interval $[x_1', x_+[$ and $]x_-, x_1']$, respectively (hence the zero x_1' is counted both in m_+ and m_-). Denote by $\zeta_+(x)$ the function defined by relations (11a) and (11b), with x_0 being replaced by x_+. In virtue of Theorem 7, there exists a constant $c_+ \geq 0$ (independent of n) such that

$$|\zeta_+(x_1') - \hbar_n^{2/3} a_{m_+}| \leq \frac{c_+ \hbar_n}{m_+^{1/3}}$$

for all $n \geq n_0$. An application of the mean value theorem,

$$|u^{3/2} - v^{3/2}| \leq \frac{3}{2} \left(\max\{u, v\}\right)^{1/2} |u - v| \quad \text{for } u > 0, v > 0,$$

yields the inequality

$$\left| |\zeta_+(x_1')|^{3/2} - \hbar_n |a_{m_+}|^{3/2} \right| \leq \frac{3}{2} \left(\frac{3}{2} \int_{x_-}^{x_+} \sqrt{E - V(x)}\, \mathrm{d}x \right)^{1/3} \frac{c_+ \hbar_n}{m_+^{1/3}} \tag{22}$$

which is valid for all sufficiently large n. Analogously, for the other turning point we get the estimate

$$\left| |\zeta_-(x_1')|^{3/2} - \hbar_n |a_{m_-}|^{3/2} \right| \leq \frac{3}{2} \left(\frac{3}{2} \int_{x_-}^{x_+} \sqrt{E - V(x)}\, \mathrm{d}x \right)^{1/3} \frac{c_- \hbar_n}{m_-^{1/3}} \tag{23}$$

where again $c_- \geq 0$ is a constant independent of n. Set

$$c = \left(\frac{3}{2} \int_{x_-}^{x_+} \sqrt{E - V(x)}\, \mathrm{d}x \right)^{1/3} \max\{c_-, c_+\}.$$

Combining (22) and (23) we arrive at the inequality

$$\left|\frac{1}{\hbar_n}\int_{x_-}^{x_+}\sqrt{E-V(x)}\,\mathrm{d}x-\frac{2}{3}\left(|a_{m_-}|^{3/2}+|a_{m_+}|^{3/2}\right)\right|\leq c\left(\frac{1}{m_-^{1/3}}+\frac{1}{m_+^{1/3}}\right).$$

Let $m=m(n)$ be the number of zeroes of $\psi_n(x)$. Obviously, $m=m_-+m_+-1$. Recalling the asymptotic behavior of $\hbar_n$, as stated in (20) (see also (18)), as well as the asymptotic formulas (21) for the roots of the Airy functions we finally find that

$$\left|n-m+O(n^{-1})-3\left(m_--\frac{1}{4}\right)-3\left(m_+-\frac{1}{4}\right)\right|\leq\frac{c}{\pi}\left(\frac{1}{m_-^{1/3}}+\frac{1}{m_+^{1/3}}\right).$$

By Theorem 7, both m_- and m_+ tend to infinity as n tends to infinity. This implies that $m(n)=n$ for all sufficiently large n and therefore, in virtue of Theorem 2, E is the nth eigenvalue of the Hamiltonian $H(\hbar_n)$ (with the numbering starting from $n=0$).

All estimates can be carried out in a uniform manner for E being replaced by λ running over some neighborhood of E. We conclude that

with the assumptions on $V(x)$ formulated in the Introduction, there exist $n_0\in\mathbb{N}$ and a neighborhood U_E of E such that for all $n\geq n_0$ and $\lambda\in U_E$, λ equals exactly the nth eigenvalue of $H\big(\hbar_n(\lambda)\big)$ (with $\hbar_n(\lambda)$ introduced in Theorem 6).

6 Proof of the formula

Here we prove the limit (6). We know that there exists a sequence of positive numbers, $\{\hbar_n\}_{n=n_0}^{\infty}$, such that E is the nth eigenvalue of $H(\hbar_n)$ (Theorem 6). This sequence is strictly decreasing and tends to 0. We even known that $\hbar_n\sim n^{-1}$ as $n\to\infty$ (see (20)). Therefore everywhere in what follows the symbol $O(\hbar)$ should be understood as a substitute for $O(n^{-1})$.

Let us fix $x_1,x_1',x_1''\in\,]x_-,x_+[$, $x_1'<x_1<x_1''$. For a given $\hbar=\hbar_n$ we shall denote by ψ a conveniently normalized eigenfunction corresponding to the eigenvalue $E=E_n$. Hence ψ is recessive both at $+\infty$ and $-\infty$. The normalization is fixed by requiring the eigenfunction ψ to coincide on the interval $]x_1',+\infty[$ with the solution described in Theorem 5 (with $f(x)=V(x)-E$ and $x_0=x_+$ being the single turning point in this interval). Theorem 5 is also applicable to the interval $]-\infty,x_1''[$ containing the turning point x_-. On this interval, ψ equals κ times the solution described in Theorem 5 for some $\kappa\in\mathbb{C}\setminus\{0\}$.

There exists a neighborhood of E, $U_E=]E_-,E_+[$, such that any $\lambda\in U_E$ satisfies the same assumptions as those imposed on E. Recall that we have fixed $k\in\mathbb{Z}$. For all sufficiently large n, the $(n+k)$th eigenvalue of $H(\hbar_n)$, called E_{n+k}, exists and lies in U_E. For brevity we shall denote E_{n+k} sometimes by $\tilde{E}$. We show below that $\tilde{E}-E=O(\hbar)$, see (24). The eigenfunction of $H(\hbar_n)$ corresponding to the eigenvalue $\tilde{E}=E_{n+k}$ and coinciding on $]x_1',+\infty[$ with the solution from Theorem 5 will be denoted by $\tilde{\psi}$. In this case, too, there exists $\tilde{\kappa}\in\mathbb{C}\setminus\{0\}$ such that on the interval $]-\infty,x_1''[$, $\tilde{\psi}$ equals

$\tilde{\kappa}$ times the solution from Theorem 5. Furthermore, denote by $\tilde{x}_\pm$ the turning points corresponding to $\tilde{E}$, i.e., $V(\tilde{x}_\pm) = \tilde{E}$. Since $V(\tilde{x}_\pm) - V(x_\pm) = \tilde{E} - E$ and $V'(x_\pm) \neq 0$ it is clear that $\tilde{x}_\pm - x_\pm = O(\hbar)$ as well.

The verification of (6) is based on a series of estimates relying on Theorem 5. This will be done in several steps.

(1) Relation between $\tilde{E}$ and E. Let $E_m(\hbar)$ be the mth eigenvalue of $H(\hbar)$. From the perturbation theory [11] one deduces that if it exists and lies below V_∞ then $E_m(\hbar)$ is strictly increasing and real analytic as a function of $\hbar$. According to the conclusion of Section 5, $E_m(\hbar)$ and $\hbar_m(\lambda)$ are mutually inverse functions. Therefore if $\hbar = \hbar_n(E)$ then $\hbar = \hbar_{n+k}(\tilde{E})$. Thus we have

$$\hbar_n(E) = \hbar_{n+k}(\tilde{E})$$

and from the asymptotic formula (20) we get

$$(2n + 2k + 1)J(E) - (2n + 1)J(\tilde{E}) = O(n^{-1}).$$

Since

$$J(\tilde{E}) = J(E) + \frac{\partial J(E)}{\partial \lambda}(\tilde{E} - E) + O((E' - E)^2)$$

we finally arrive at the equation

$$\frac{2k}{2n+1}\,\frac{J(E)}{T(E)} - \tilde{E} + E = O(n^{-2}) + O((\tilde{E} - E)^2)$$

whose solution satisfies

$$\tilde{E} = E + \frac{J(E)}{T(E)}\,\frac{k}{n} + O(n^{-2}). \tag{24}$$

(2) Asymptotic behavior of κ and $\tilde{\kappa}$. On the interval $]x'_1, x''_1[$ one can compare the asymptotics of the solutions which are respectively recessive at $+\infty$ and $-\infty$ and infer this way the asymptotic behavior of κ as $\hbar \to 0$. For a moment we shall distinguish by a subscript the functions $\zeta_\pm$ related to the turning points $x_\pm$ and defined respectively on the intervals $[x'_1, +\infty[$ and $]-\infty, x''_1]$. Thus

$$\frac{2}{3}\,|\zeta_+|^{2/3} = \left|\int_{x_+}^{x} |f(t)|\,\mathrm{d}t\right|, \quad \frac{2}{3}\,|\zeta_-|^{2/3} = \left|\int_{x}^{x_-} |f(t)|\,\mathrm{d}t\right|,$$

and both ζ_+/f and ζ_-/f are positive functions on their domains. We have

$$\psi(x) = \left(\frac{\zeta_+}{f}\right)^{1/4} \left(\mathrm{Ai}(\hbar^{-2/3}\zeta_+) + \varepsilon_+(\hbar, x)\right)$$

for $x \geq x'_1$, and

$$\psi(x) = \kappa \left(\frac{\zeta_-}{f}\right)^{1/4} \left(\mathrm{Ai}(\hbar^{-2/3}\zeta_-) + \varepsilon_-(\hbar, x)\right)$$

for $x \leq x_1''$. Suppose that $x \in [x_1', x_1'']$. Recalling that

$$\operatorname{Ai}(-z) = \frac{1}{\pi^{1/2} z^{1/4}} \left(\cos\left(\frac{2}{3}\, z^{3/2} - \frac{\pi}{4} \right) + O(z^{-3/2}) \right) \quad \text{as } z \to +\infty \tag{25}$$

and the error term estimates from Theorem 5 we arrive at the equality

$$\cos\left(\frac{2}{3}\, \hbar^{-1} |\zeta_+|^{3/2} - \frac{\pi}{4} \right) + O(\hbar) = \kappa \left(\cos\left(\frac{2}{3}\, \hbar^{-1} |\zeta_-|^{3/2} - \frac{\pi}{4} \right) + O(\hbar) \right).$$

Furthermore, in virtue of (20) it holds

$$\frac{2}{3}\, \hbar^{-1} \left(|\zeta_+|^{2/3} + |\zeta_-|^{2/3} \right) = \hbar^{-1} \int_{x_-}^{x_+} |f(t)| \, \mathrm{d}t = \left(n + \frac{1}{2} \right) \pi + O(\hbar).$$

Combining the last two equalities we find that

$$\cos\left(\frac{2}{3}\, \hbar^{-1} |\zeta_+|^{3/2} - \frac{\pi}{4} \right) + O(\hbar) = \kappa \left((-1)^n \cos\left(\frac{2}{3}\, \hbar^{-1} |\zeta_+|^{3/2} - \frac{\pi}{4} \right) + O(\hbar) \right).$$

For $\hbar$ sufficiently small it clearly exists $x \in [x_1', x_1'']$ such that

$$\cos\left(\frac{2}{3}\, \hbar^{-1} |\zeta_+|^{3/2} - \frac{\pi}{4} \right) = 1.$$

It follows immediately that

$$\kappa = (-1)^n + O(\hbar). \tag{26}$$

Similarly,

$$\tilde{\kappa} = (-1)^{n+k} + O(\hbar). \tag{27}$$

(3) The leading asymptotic term on the interval $]x_+ - \delta, \infty[$. Fix $\delta > 0$ sufficiently small (at least $x_1 < x_+ - \delta$). Let us show that

$$\int_{x_+ - \delta}^{\infty} \psi^2 \, \mathrm{d}x = \delta^{1/2} O(\hbar^{1/3}), \quad \int_{-\infty}^{x_- + \delta} \psi^2 \, \mathrm{d}x = \delta^{1/2} O(\hbar^{1/3}). \tag{28}$$

We shall verify only the first equality in (28). In view of (26) and (27), the verification of the second one is analogous.

Here and everywhere in what follows the symbol $O(\hbar^{\varepsilon})$ should be interpreted properly. It means that there exists a constant $c \geq 0$ (independent of δ) and $\hbar_0(\delta) > 0$ such that for all $\hbar$, $0 < \hbar < \hbar_0(\delta)$, it holds $|O(\hbar^{\varepsilon})| \leq c\hbar^{\varepsilon}$.

First let us estimate the contribution from the leading asymptotic term of ψ. Applying the substitution $x = \xi(\hbar^{2/3} z)$ we get the expression

$$\int_{x_+ - \delta}^{\infty} \left(\frac{\zeta}{f} \right)^{1/2} \operatorname{Ai}(\hbar^{-2/3} \zeta)^2 \, \mathrm{d}x = \hbar^{4/3} \int_{\hbar^{-2/3} \zeta(x_+ - \delta)}^{\infty} \frac{z}{f\big(\xi(\hbar^{2/3} z)\big)} \operatorname{Ai}(z)^2 \, \mathrm{d}z. \tag{29}$$

By the assumptions, there exist $x_2 > x_+$ and $c_1 > 0$ such that $f(x) \geq c_1$ for $x \geq x_2$. The function $\zeta(x)/f(x)$ is continuous on the interval $[x_1, x_2]$ and therefore it is majorized on this interval by a constant $c_2 \geq 0$. This also means that

$$0 < \frac{y}{f\big(\xi(y)\big)} \leq c_2 \quad \text{for } \zeta(x_1) \leq y \leq \zeta(x_2).$$

This way we get the following upper bound on (29), namely

$$\begin{aligned}
&\hbar^{2/3} \int_{\hbar^{-2/3}\zeta(x_+-\delta)}^{\hbar^{-2/3}\zeta(x_2)} c_2 \operatorname{Ai}(z)^2 \,\mathrm{d}z + \hbar^{4/3} \int_{\hbar^{-2/3}\zeta(x_2)}^{\infty} \frac{z}{c_1} \operatorname{Ai}(z)^2 \,\mathrm{d}z \\
&\leq c_2 \hbar^{2/3} \big(\operatorname{Ai}'(x)^2 - x \operatorname{Ai}(x)^2\big)\Big|_{x=\hbar^{-2/3}\zeta(x_+-\delta)} + o(\hbar^{4/3}).
\end{aligned}$$

Here we have used the knowledge of the primitive function

$$\int \operatorname{Ai}(x)^2 \,\mathrm{d}x = x \operatorname{Ai}(x)^2 - \operatorname{Ai}'(x)^2.$$

In addition to formula (25) let us recall also the asymptotic behavior of the derivative of the Airy function,

$$\operatorname{Ai}'(-z) = \frac{z^{1/4}}{\pi^{1/2}} \left(\sin\!\left(\frac{2}{3}\, z^{3/2} - \frac{\pi}{4} \right) + O(z^{-3/2}) \right) \quad \text{as } z \to +\infty. \tag{30}$$

Since $\zeta(x_+ - \delta) = -\zeta'(y)\delta$ for some $y \in [x_+ - \delta, x_+]$ we find that for $x = \hbar^{-2/3}\zeta(x_+ - \delta)$ it holds

$$|\hbar^{2/3} \operatorname{Ai}'(x)^2| \leq \text{const}\, \hbar^{2/3} \left(\hbar^{-2/3}\delta\right)^{1/2} = \text{const}\, \hbar^{1/3}\delta^{1/2}$$

and

$$|\hbar^{2/3} x \operatorname{Ai}(x)^2| \leq \text{const}\, \hbar^{2/3}\hbar^{-2/3}\delta \left(\hbar^{-2/3}\delta\right)^{-1/2} = \text{const}\, \hbar^{1/3}\delta^{1/2}.$$

We have shown that

$$\int_{x_+-\delta}^{\infty} \left(\frac{\zeta}{f}\right)^{1/2} \operatorname{Ai}(\hbar^{-2/3}\zeta)^2 \,\mathrm{d}x = \delta^{1/2} O(\hbar^{1/3}).$$

(4) The error term on the interval $]x_+ - \delta, \infty[$. Further let us write

$$\psi^2 = \left(\frac{\zeta}{f}\right)^{1/2} \operatorname{Ai}(\hbar^{-2/3}\zeta)^2 + \varepsilon_2(\hbar, x).$$

It is known that

$$\operatorname{Ai}(x) \leq \frac{1}{2\sqrt{\pi}}\, x^{-1/4} \exp\!\left(-\frac{2}{3}\, \hbar^{-1} x^{3/2} \right) \quad \text{for } x > 0,$$

see [13, Chapter 11]. Using also the estimates of error terms from Theorem 5 one can check that

$$|\varepsilon_2(\hbar, x)| \leq \text{const}\, f^{-1/2} \exp\!\left(-\frac{4}{3}\, \hbar^{-1} \zeta^{3/2} \right) \hbar^{4/3} \quad \mathit{for}\ x > x_+.$$

It follows that

$$\begin{aligned}\left|\int_{x_+}^{\infty}\varepsilon_2(\hbar,x)\,\mathrm{d}x\right| &\leq \mathrm{const}\,\hbar^{4/3}\int_{x_+}^{\infty} f^{-1/2}\exp\!\left(-\frac{4}{3}\,\hbar^{-1}\zeta^{3/2}\right)\mathrm{d}x\\ &= \mathrm{const}\,\hbar^{4/3}\int_0^{\infty}\frac{y^{1/2}}{f\big(\xi(y)\big)}\,\exp\!\left(-\frac{4}{3}\,\hbar^{-1}y^{3/2}\right)\mathrm{d}y. \qquad (31)\end{aligned}$$

There exists $c \geq 0$ such that for $y > 0$, $f\big(\xi(y)\big)^{-1} \leq c(1+y^{-1})$. Hence (31) is majorized by

$$\mathrm{const}\,\hbar^{4/3}\int_0^{\infty}(y^{1/2}+y^{-1/2})\exp\!\left(-\frac{4}{3}\,\hbar^{-1}y^{3/2}\right)\mathrm{d}y = O(\hbar^{5/3}).$$

The asymptotic formula (25) implies that $|\,\mathrm{Ai}(x)| \leq \mathrm{const}\,|x|^{-1/4}$ for $x < 0$. Recalling once more Theorem 5 we have

$$\left|\int_{x_1}^{x_+}\varepsilon_2(\hbar,x)\,\mathrm{d}x\right| \leq \mathrm{const}\,\hbar^{4/3}\int_{x_1}^{x_+}|f|^{-1/2}\,\mathrm{d}x = O(\hbar^{4/3}). \qquad (32)$$

This concludes the verification of (28).
(5) Oscillating integral on the interval $]x_1, x_+-\delta[$. By the usual integration by parts one can verify the following claim.
Let $[a,b]$ *be a compact interval,* $F \in C^1([a,b])$, $\mu \in C^2([a,b])$ *and* $\nu(\hbar,z)$ *be twice continuously differentiable in* z *on* $[a,b]$. *Assume that* $\mu'(z)$ *nowhere vanishes on* $[a,b]$ *and*

$$\sup_{z\in[a,b]}|\partial_z\nu(\hbar,z)| = O(1),\ \ \sup_{z\in[a,b]}|\partial_z^2\nu(\hbar,z)| = O(1).$$

Then for all sufficiently small $\hbar$ *it holds true that*

$$\left|\int_a^b F(z)\sin\!\big(\hbar^{-1}\mu(z)+\nu(\hbar,z)\big)\,\mathrm{d}z\right| \leq \mathrm{const}\,\hbar$$

where the constant depends only on the length of the interval $[a,b]$ *and on the quantities*

$$\mu_0^{-1}\|F\|_C,\ \mu_0^{-2}\|F\|_C\|\mu''\|_C,\ \mu_0^{-1}\|F'\|_C,$$

with

$$\mu_0 = \min_{z\in[a,b]}|\mu'(z)|$$

and $\|\cdot\|_C$ *standing for the norm in the Banach space* $C([a,b])$.

As a consequence we find that if $W \in C^1(\mathbb{R})$ then

$$\int_{x_1}^{x_+-\delta}\frac{W}{\sqrt{E-V}}\,\sin\!\left(\frac{2}{3}\,\hbar^{-1}\big(|\zeta|^{3/2}+|\tilde\zeta|^{3/2}\big)\right)\mathrm{d}x = \delta^{-1}O(\hbar). \qquad (33)$$

To show this asymptotics it suffices to set in the above claim $F = W/\sqrt{E-V}$, $\mu = (4/3)|\zeta|^{3/2}$ and

$$\begin{aligned}\nu(\hbar,z) &= \frac{2}{3}\,\hbar^{-1}\big(|\tilde\zeta(z)|^{3/2}-|\zeta(z)|^{3/2}\big)\\ &= \hbar^{-1}\left(\int_z^{\tilde x_+}\sqrt{\tilde E-V(t)}\,\mathrm{d}t-\int_z^{x_+}\sqrt{E-V(t)}\,\mathrm{d}t\right).\end{aligned}$$

Hence $\mu'(z) = -2\sqrt{E - V(z)}$ and

$$\begin{aligned}
\partial_z \nu(\hbar, z) &= \frac{E - \tilde{E}}{\hbar} \left(\sqrt{E - V(z)} + \sqrt{\tilde{E} - V(z)} \right)^{-1}, \\
\partial_z^2 \nu(\hbar, z) &= \frac{E - \tilde{E}}{2\hbar} V'(z) \big(E - V(z)\big)^{-1/2} \big(\tilde{E} - V(z)\big)^{-1/2} \\
&\quad \times \left(\sqrt{E - V(z)} + \sqrt{\tilde{E} - V(z)} \right)^{-1}.
\end{aligned}$$

(6) The leading asymptotic term on the interval $]x_1, x_+ - \delta[$. Let us check the contribution to the matrix element coming from the interval $[x_1, x_+ - \delta]$. The leading asymptotic term in the expansion of ψ is given in (16). We also need the asymptotic behavior of the Airy function (25) and the fact that the function f/ζ is continuous and hence bounded on the interval $[x_1, x_+]$. We conclude that

$$\psi \sim \left(\frac{\zeta}{f}\right)^{1/4} \mathrm{Ai}(\hbar^{-2/3}\zeta) = \frac{\hbar^{1/6}}{\sqrt{\pi}\,|f|^{1/4}} \cos\!\left(\frac{2}{3}\,\hbar^{-1}|\zeta|^{3/2} - \frac{\pi}{4}\right) + \frac{1}{|f|^{7/4}}\, O(\hbar^{7/6}).$$

Observe that

$$\hbar^{4/3} \int_{x_1}^{x_+ - \delta} \frac{\mathrm{d}x}{|f|^2} = \delta^{-1} O(\hbar^{4/3}),$$

and on the interval $[x_1, x_+ - \delta]$,

$$(\tilde{E} - V)^{-1/4} = (E - V)^{-1/4}\big(1 + \delta^{-1} O(\hbar)\big).$$

From the boundedness of W and from an estimate similar to (32) it follows that

$$\begin{aligned}
\int_{x_1}^{x_+ - \delta} W \psi \tilde{\psi}\, \mathrm{d}x &= \int_{x_1}^{x_+ - \delta} W \left(\frac{\zeta}{f}\right)^{1/4} \left(\frac{\tilde{\zeta}}{f}\right)^{1/4} \mathrm{Ai}(\hbar^{-2/3}\zeta)\, \mathrm{Ai}(\hbar^{-2/3}\tilde{\zeta})\, \mathrm{d}x + O(\hbar^{4/3}) \\
&= \frac{\hbar^{1/3}}{\pi} \int_{x_1}^{x_+ - \delta} \frac{W}{|f|^{1/2}} \left(1 + \delta^{-1} O(\hbar)\right) \\
&\qquad \times \cos\!\left(\frac{2}{3}\,\hbar^{-1}|\zeta|^{3/2} - \frac{\pi}{4}\right) \cos\!\left(\frac{2}{3}\,\hbar^{-1}|\tilde{\zeta}|^{3/2} - \frac{\pi}{4}\right) \mathrm{d}x \\
&\quad + \delta^{-1} O(\hbar^{4/3}).
\end{aligned}$$

Using the asymptotic behavior (33) we have

$$\int_{x_1}^{x_+ - \delta} W \psi \tilde{\psi}\, \mathrm{d}x = \frac{\hbar^{1/3}}{2\pi} \int_{x_1}^{x_+ - \delta} \frac{W}{\sqrt{E - V}} \cos\!\left(\frac{2}{3}\,\hbar^{-1}(|\zeta|^{3/2} - |\tilde{\zeta}|^{3/2})\right) \mathrm{d}x + \delta^{-1} O(\hbar^{4/3}). \tag{34}$$

(7) The argument of the cosine on the interval $]x_1, x_+ - \delta[$. Let us show that for $x \in [x_1, x_+ - \delta]$,

$$\frac{2}{3}\,\hbar^{-1}(|\zeta|^{3/2} - |\tilde{\zeta}|^{3/2}) = -\frac{2\pi k}{T}\,\tau(x) + \delta^{1/2} O(1) \tag{35}$$

where $\tau(x)$ was defined in (8). We have

$$\begin{aligned}
\frac{2}{3}\,\hbar^{-1}(|\zeta|^{3/2}-|\tilde{\zeta}|^{3/2}) &= \hbar^{-1}\left(\int_x^{x_+}\sqrt{E-V}\,\mathrm{d}t-\int_x^{\tilde{x}_+}\sqrt{\tilde{E}-V}\,\mathrm{d}t\right)\\
&= \hbar^{-1}\bigg(\int_x^{x_+-\delta}\left(\sqrt{E-V}-\sqrt{\tilde{E}-V}\right)\mathrm{d}t\\
&\qquad +\int_{x_+-\delta}^{x_+}\sqrt{E-V}\,\mathrm{d}t-\int_{x_+-\delta}^{\tilde{x}_+}\sqrt{\tilde{E}-V}\,\mathrm{d}t\bigg).
\end{aligned}$$

Set temporarily

$$g(y)=\int_{x_+-\delta}^{y}\sqrt{V(y)-V(t)}\,\mathrm{d}t.$$

Then for y lying between x_+ and $\tilde{x}_+$ it holds

$$\begin{aligned}
|g'(y)| &= \left|\frac{1}{2}\int_{x_+-\delta}^{y}\frac{V'(y)}{\sqrt{V(y)-V(t)}}\,\mathrm{d}t\right|\le\frac{1}{2}\,\mathrm{const}\int_{x_+-\delta}^{y}\frac{\mathrm{d}t}{\sqrt{y-t}}\\
&\le \mathrm{const}\,\sqrt{|x_+-\tilde{x}_+|+\delta}.
\end{aligned}$$

Hence

$$\begin{aligned}
\left|\int_{x_+-\delta}^{x_+}\sqrt{E-V}\,\mathrm{d}t-\int_{x_+-\delta}^{\tilde{x}_+}\sqrt{\tilde{E}-V}\,\mathrm{d}t\right| &= |g(x_+)-g(\tilde{x}_+)|\\
&\le \mathrm{const}\,\sqrt{|x_+-\tilde{x}_+|+\delta}\,|x_+-\tilde{x}_+|\\
&= \delta^{1/2}O(\hbar). \qquad (36)
\end{aligned}$$

Furthermore,

$$\begin{aligned}
\sqrt{E-V}-\sqrt{\tilde{E}-V}-\frac{E-\tilde{E}}{2\sqrt{E-V}} &= \frac{(E-\tilde{E})^2}{2\left(\sqrt{E-V}+\sqrt{\tilde{E}-V}\right)^2\sqrt{E-V}}\\
&\le \frac{(E-\tilde{E})^2}{2(E-V)^{3/2}}
\end{aligned}$$

and

$$\int_x^{x_+-\delta}\frac{(E-\tilde{E})^2}{(E-V)^{3/2}}\,\mathrm{d}t=\delta^{-1/2}O(\hbar^2).$$

From (24) it follows that

$$\hbar^{-1}(\tilde{E}-E)=\frac{2\pi k}{T}+O(\hbar)$$

where T is the period of the classical motion, see (7). Altogether this means that

$$\begin{aligned}
\hbar^{-1}\int_x^{x_+-\delta}\left(\sqrt{E-V}-\sqrt{\tilde{E}-V}\right)\mathrm{d}t &= -\left(\frac{2\pi k}{T}+O(\hbar)\right)\int_x^{x_+-\delta}\frac{\mathrm{d}t}{2\sqrt{E-V(t)}} \\
&\quad + \delta^{-1/2}O(\hbar) \\
&= -\frac{2\pi k}{T}\int_x^{x_+}\frac{\mathrm{d}t}{2\sqrt{E-V(t)}} \\
&\quad + \delta^{1/2}O(1)+\delta^{-1/2}O(\hbar).
\end{aligned} \tag{37}$$

Relations (36) and (37) jointly imply (35).

(8) The final step. From (34) and (35) we derive that

$$\begin{aligned}
\int_{x_1}^{x_+-\delta} W\psi\tilde{\psi}\,\mathrm{d}x &= \frac{\hbar^{1/3}}{2\pi}\Bigg(\int_{x_1}^{x_+-\delta}\frac{W(x)}{\sqrt{E-V(x)}} \\
&\qquad \times\cos\!\left(\frac{2\pi k}{T}\,\tau(x)+\delta^{1/2}O(1)+\delta^{-1/2}O(\hbar)\right)\mathrm{d}x+\delta^{-1}O(\hbar)\Bigg) \\
&= \frac{\hbar^{1/3}}{2\pi}\left(\int_{x_1}^{x_+}\frac{W(x)}{\sqrt{E-V(x)}}\cos\!\left(\frac{2\pi k}{T}\,\tau(x)\right)\mathrm{d}x+\delta^{1/2}O(1)\right).
\end{aligned} \tag{38}$$

The interval $[x_-+\delta,x_1]$ can be treated similarly. We have

$$\int_{x_-+\delta}^{x_1} W\psi\tilde{\psi}\,\mathrm{d}x = \kappa\tilde{\kappa}\,\frac{\hbar^{1/3}}{2\pi}\left(\int_{x_-}^{x_1}\frac{W(x)}{\sqrt{E-V(x)}}\cos\!\left(\frac{2\pi k}{T}\,\tau_-(x)\right)\mathrm{d}x+\delta^{1/2}O(1)\right)$$

where

$$\tau_-(x)=\frac{1}{2}\int_{x_-}^{x}\frac{\mathrm{d}y}{\sqrt{E-V(y)}}=\frac{1}{2}T-\tau(x).$$

Taking into account also (26) and (27) we finally find that

$$\int_{x_-+\delta}^{x_1} W\psi\tilde{\psi}\,\mathrm{d}x = \frac{\hbar^{1/3}}{2\pi}\left(\int_{x_-}^{x_1}\frac{W(x)}{\sqrt{E-V(x)}}\cos\!\left(\frac{2\pi k}{T}\,\tau(x)\right)\mathrm{d}x+\delta^{1/2}O(1)\right). \tag{39}$$

From the boundedness of W and relations (28), (38) and (39) it follows that

$$\int_{\mathbb{R}} W\psi\tilde{\psi}\,\mathrm{d}x = \frac{\hbar^{1/3}}{2\pi}\left(\int_0^T W\big(q(t)\big)e^{ik\omega t}\,\mathrm{d}t+\delta^{1/2}O(1)\right). \tag{40}$$

As a particular case, with $W(x)=1$ and $k=0$, we have

$$\int_{\mathbb{R}}\psi^2\,\mathrm{d}x=\frac{\hbar^{1/3}}{2\pi}\big(T+\delta^{1/2}O(1)\big). \tag{41}$$

The same relation holds also for the squared norm of $\tilde{\psi}$.

Relations (40) and (41) imply that there exists $c\geq 0$ such that for all sufficiently small positive δ and all n, $n\geq n_0(\delta)$, it holds

$$\left|\langle n|W(x)|n+k\rangle-\frac{1}{T}\int_0^T W(q(t))\,e^{ik\omega t}\mathrm{d}t\right|\leq c\delta^{1/2}.$$

Since δ is arbitrary this concludes the verification of the limit (6).

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References

[1] J. Bellissard: in *Trends and Developments in the Eighties*, Albeverio and Blanchard Eds., Word Scientific, Singapore 1985, pp. 1–106.

[2] J. Bellissard and M. Vittot: *Ann. Inst. Henri Poincaré* **52**, 175 (1990).

[3] F. A. Berezin and M. A. Shubin: *The Schrödinger Equation*, Moscow University Press, Moscow 1983 (in Russian). English transl. Kluwer, Dordrecht 1991.

[4] R. Brummelhuis and A. Uribe: *Commun. Math. Phys.* **136**, 567 (1991).

[5] A.-M. Charbonnel: *Ann. Inst. Henri Poincaré* **56**, 187 (1992).

[6] M. Combescure and D. Robert: *Ann. Inst. Henri Poincaré* **61**, 443 (1994).

[7] S. De Bièvre and J. Renaud: *J. Phys. A: Math. Gen.* **29**, L585 (1996).

[8] P. Duclos, O. Lev, P. Šťovíček and M. Vittot: *Rev. Math. Phys.* **14**, 531 (2002).

[9] M. Feingold and A. Peres: *Phys. Rev. A* **34**, 591 (1986).

[10] M. Gutzwiller: *J. Math. Phys.* **12**, 343 (1971).

[11] T. Kato: *Perturbation Theory of Linear Operators*, Springer-Verlag, New York 1966.

[12] L. D. Landau and E. M. Lifshitz: *Quantum Mechanics*, Pergamon Press, London 1958.

[13] F. W. J. Olver: *Asymptotics and Special Functions*, Academic Press, New York 1974.

[14] T. Paul and A. Uribe: *Ann. Inst. Henri Poincaré* **59**, 357 (1993).

[15] N. Ripamonti: *J. Phys. A: Math. Gen.* **29**, 5137 (1996).

[16] N. Ripamonti: *Math. Phys. Electronic J.* **4**, paper 2 (1998).

[17] M. Reed and B. Simon: *Methods of Modern Mathematical Physics IV*, Academic Press, New York 1978.

[18] D. Robert: *Helv. Phys. Acta* **71**, 44 (1998).

[19] S. Zelditch : *J. Funct. Anal.* **94**, 415 (1990).