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Tunneling by a semiclassical initial value method with higher order corrections

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Abstract

Tunneling through the one-dimensional Eckart barrier is treated by applying a higher order semiclassical approximation which adds corrections proportional to powers of $\hbar$ to the Herman–Kluk (HK) initial value approximation. Although the usual, zero-order HK treatment is very poor in this case, the first- and second-order corrections substantially improve the accuracy of the computed tunneling probabilities. To investigate how this works, the HK expression is shown to be equivalent, for the present purposes, to a formula involving a single integral over the initial momentum, with an integrand that has a simple analytical form. Similarly, the most important part of the first-order correction term is shown to be expressible in a very simple form. For a particular range of energies, the integral can be analyzed in terms of a steepest descent treatment along a path through a caustic. In this way, it is verified that the zero-order approximation does not approach the correct classical limit as $\hbar \to 0$, but the first-order term, which does not vanish in this limit, improves the accuracy of the result. More generally, the corrections of each order contain terms that are of all orders in $\hbar^{1/3}$, including those that are $O(\hbar^0)$ and which survive in the classical limit. The infinite sum over such terms is performed analytically and shown to yield the correct classical limit for the tunneling amplitude.

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(Some figures in this article are in colour only in the electronic version)

1. Introduction

Semiclassical initial value representation (IVR) methods [1–3] approximate the quantum propagator as an integral over phase space. Points (p, q) in this space are treated as initial conditions for ordinary real-valued classical trajectories which are used to construct various quantities appearing in the integrand. Although several varieties of IVR methods exist [1], the approximation developed by Herman and Kluk (HK) [4, 5], which associates a harmonic oscillator coherent state wavefunction with each trajectory, appears to be the most convenient and accurate for general applications. In addition to practical computational advantages over the more familiar semiclassical (SC) treatment of Van Vleck [6] and Gutzwiller [7] (VVG), the HK and related expressions yield improved accuracy due to their nature as uniform asymptotic approximations to the quantum propagator.

Despite many successes, IVR methods encounter problems in the treatment of tunneling between separate classically allowed regions [8–14]. For example, calculations of tunneling through one-dimensional barriers give probabilities that may be in error by orders of magnitude when these probabilities become small. Such problems were analyzed in [15] which investigated tunneling through the one-dimensional Eckart barrier using an IVR approximation related to the HK method. The reason for the inaccuracy of the approximation was shown to be related to effects of caustic points in phase space at which a pre-exponential factor in the integrand vanishes. It was shown how these problems could be overcome by a judicious choice of the width of the coherent state wavefunctions in the IVR treatment. This moves the caustics far enough from the real axis so they do not strongly affect the tunneling calculation. The resulting approximation may then become accurate because, in effect, the integrals in the IVR expressions allow the initial values of the trajectories to be analytically continued to the complex plane, resulting in dynamics that would be forbidden for real trajectories. Related works, confirming the ability of real trajectories to describe tunneling semiclassically, have since appeared in the contexts of both IVR [16] and non-IVR [17] methods.

Although the treatment of the IVR tunneling problem presented in [15] produced accurate tunneling probabilities for the Eckart system, its application to more general cases is difficult since it requires a separate, thorough, study of the classical dynamics for each system treated and it is not clear how to extend the method to systems having more than one degree of freedom. Therefore, more general techniques for the treatment of tunneling by IVR methods are clearly needed.

One approach that might lead to a more robust description of tunneling involves introducing semiclassical corrections to the HK approximation. A systematic method for obtaining such corrections was presented in a recent work [18] which derived the HK approximation as the lowest order asymptotic solution to the Schrödinger equation for the propagator in the limit as $\hbar \to 0$. This treatment, which we refer to as the higher order HK (HOHK) method, provides equations that can be solved to determine higher order terms in the semiclassical expansion for the propagator, making it formally possible to correct the HK approximation to arbitrary order in $\hbar$.

An attempt to treat tunneling by this approach may, nevertheless, appear to be misguided. The method described above modifies only the *expression* for the propagator; it does not modify the ordinary, real, classical trajectories that are used to calculate this expression. Such trajectories remain unable to execute classically forbidden motion. For this reason, it is futile to attempt to treat tunneling by adding analogous correction terms [19, 20] to expressions based on the Wentzel–Brillouin–Kramers (WKB) wavefunction or the VVG propagator with real-valued trajectories. However, as mentioned above, the possibility that IVR methods may treat tunneling is based on the ability of the integrals to provide an analytic continuation of the classical dynamics to complex initial conditions. Thus, the dynamics directly entering the calculations need not describe classically forbidden motion if the IVR integrand is carefully designed to allow the analytic continuation. This mechanism for analytic continuation does not exist in the straightforward application of the WKB or VVG approximations. Thus, we cannot dismiss out of hand the possibility that the semiclassical corrections to the IVR formula may enable a more accurate description of tunneling.

In previous work [21], we presented some preliminary calculations designed to test the ability of the HOHK approximation to treat the propagation of wavefunctions in a one-dimensional quartic double well system. This case is especially problematic for the uncorrected IVR methods which become highly inaccurate as soon as tunneling sets in. The results of [21] showed that the SC corrections substantially improved the accuracy of the semiclassical wavefunctions at short times. However, the corrections seemed to become less effective for longer times so that their ability to describe tunneling at such times was not decisively established.

In the present work we apply the HOHK treatment to tunneling for the case of the one-dimensional Eckart barrier, which lends itself to a simpler mathematical analysis than possible for the double-well system. We find that the corrections produce an accurate description of tunneling in an energy range that may correspond to very small tunneling probabilities. In contrast to [15], the success of this treatment does not depend on the optimization of the Gaussian width parameter in the IVR treatment. We analyze our results in some detail in order to understand how the corrections work and to explain some unexpected and unusual aspects of the $\hbar$-expansion in the present case.

Our HOHK approach should be distinguished from a treatment developed by Pollak and coworkers [22–25] which achieves a systematic improvement of the HK approximation in a different way and which has also been applied to tunneling in the Eckart system [26]. For the present purposes, it is sufficient to remark that the correction terms in Pollak's expressions have a more complicated dependence on $\hbar$ than those used in our treatment so that his expansion does not constitute a semiclassical series in the same sense as the one applied here. Other comparisons of the two treatments have been presented in [18, 21].

The remainder of this paper is organized as follows. In section 2 we review the basic equations for the HK and HOHK approximations. We apply these numerically in section 3 to calculate the tunneling probability in the Eckart system. In section 4 we simplify the equations to allow a more thorough analysis and present further calculations using the resulting expressions. In section 5, we identify some features of the results that appear to be puzzling and specify issues that need to be clarified. In section 6 we analyze the SC expressions in order to resolve these issues and to understand, in some detail, how the corrected IVR method successfully improves the description of tunneling. Finally, in section 7 we summarize and discuss the results of this work.

2. The HK and HOHK approximations

For a one-dimensional system, the HK treatment semiclassically approximates the propagator

$$K_t(x', x) = \langle x'| \exp(-\mathrm{i}\hat{H}t/\hbar)|x\rangle, \tag{2.1}$$

describing evolution of initial position x to final position x' in time t, as

$$K_t(x', x) = (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} \mathrm{d}p \int_{-\infty}^{\infty} \mathrm{d}q \exp[-\gamma_2(x' - q_t)^2/\hbar + \mathrm{i}p_t(x' - q_t)/\hbar] \\ \times R_t(p, q) \exp[\mathrm{i}S_t(p, q)/\hbar] \exp[-\gamma_1(x - q)^2/\hbar - \mathrm{i}p(x - q)/\hbar]. \tag{2.2}$$

In this expression (p_t, q_t) are values of the momentum and coordinate at time t along a classical trajectory initiated from point (p, q) in phase space, γ_1 and γ_2 are generally complex-valued parameters with positive real parts,

$$S_t(p, q) = \int_0^t [p_\tau \dot{q}_\tau - H(p_\tau, q_\tau)]\, \mathrm{d}\tau \tag{2.3}$$

is the classical action integral along a trajectory, and the HK prefactor R_t is given by

$$R_t = \left(\frac{2\gamma_1 b_t}{\pi\hbar}\right)^{1/2}, \tag{2.4}$$

where

$$b_t = \frac{1}{2}\left(\frac{\partial p_t}{\partial p} - 2\mathrm{i}\gamma_2\frac{\partial q_t}{\partial p} - \frac{1}{2\mathrm{i}\gamma_1}\frac{\partial p_t}{\partial q} + \frac{\gamma_2}{\gamma_1}\frac{\partial q_t}{\partial q}\right). \tag{2.5}$$

It is useful to express b_t in the alternative form

$$b_t = \frac{\partial p_t}{\partial z} - 2\mathrm{i}\gamma_2\frac{\partial q_t}{\partial z} \tag{2.6}$$

where

$$\frac{\partial}{\partial z} \equiv \frac{1}{2}\frac{\partial}{\partial p} - \frac{1}{4\mathrm{i}\gamma_1}\frac{\partial}{\partial q}. \tag{2.7}$$

This notation is consistent with the identification of the complex quantities defined as

$$z = p - 2\mathrm{i}\gamma_1 q \qquad \bar{z} = p + 2\mathrm{i}\gamma_1 q, \tag{2.8}$$

as independent variables.

The derivation of the HK and HOHK formulae in [18] is based on the ansatz

$$K_t(x', x) = (2\pi\hbar)^{-1}\int_{-\infty}^{\infty}\mathrm{d}p\int_{-\infty}^{\infty}\mathrm{d}q\,\exp[-\gamma_2(x' - q_t)^2/\hbar + \mathrm{i}p_t(x' - q_t)/\hbar] \\ \times k_t(p, q)\exp[-\gamma_1(x - q)^2/\hbar - \mathrm{i}p(x - q)/\hbar], \tag{2.9}$$

where the function $k_t(p, q)$ is determined by imposing the Schrödinger equation $[\mathrm{i}\hbar\partial/\partial t - \hat{H}(x')]K_t(x', x) = 0$, subject to the initial condition $K_0(x', x) = \delta(x' - x)$. After a number of steps, one obtains an asymptotic expression for k_t of the form

$$k_t(p, q) = \mathrm{e}^{\mathrm{i}S_t(p,q)/\hbar}R_t(p, q)\sum_{n\geqslant 0}\hbar^n g_t^{(n)}(p, q), \tag{2.10}$$

where $g_t^{(0)} = 1$, and the remaining $g_t^{(n)}$ obey the ordinary differential equations

$$\dot{g}_t^{(1)} = \mathrm{i}b_t^{-1/2}\tilde{L}_t^{(1)}b_t^{1/2}, \tag{2.11}$$

and, more generally,

$$\dot{g}_t^{(n)} = \mathrm{i}b_t^{-1/2}\sum_{j=1}^{n}\tilde{L}_t^{(j)}\left(b_t^{1/2}g_t^{(n-j)}\right), \qquad n = 2, 3, \ldots, \tag{2.12}$$

subject to the initial conditions $g_0^{(n)} = 0$. In these equations, $\tilde{L}_t^{(j)}$ are certain differential operators with respect to variable z that are independent of $\hbar$, and the dot denotes differentiation with respect to t. Equations (2.11)–(2.12) form a closed hierarchy that can be solved recursively to obtain terms $g_t^{(n)}$ to arbitrary order n.

It should be noted that the expression for the propagator in (2.9) reduces to the HK approximation if the series in (2.10) is truncated at the $n = 0$ term. Thus, subsequent terms, proportional to $\hbar^n$ for $n \geqslant 1$, provide SC corrections to the HK treatment. Compared to the HK approximation, (2.9) merely replaces the prefactor R_t with $R_t\sum\hbar^n g_t^{(n)}$. Alternatively, (2.9) replaces the HK expression with the series

$$K_t(x', x) = \sum_{n\geqslant 0}\hbar^n K_t^{(n)}(x', x), \tag{2.13}$$

where $K_t^{(0)}$ is the HK propagator and the quantities

$$K_t^{(n)}(x',x) = (2\pi\hbar)^{-1}\int_{-\infty}^{\infty}\mathrm{d}p\int_{-\infty}^{\infty}\mathrm{d}q\,\exp[-\gamma_2(x'-q_t)^2/\hbar + \mathrm{i}p_t(x'-q_t)/\hbar]R_t(p,q)$$
$$\times\, g_t^{(n)}(p,q)\exp[\mathrm{i}S_t(p,q)/\hbar]\exp[-\gamma_1(x-q)^2/\hbar - \mathrm{i}p(x-q)/\hbar] \qquad (2.14)$$

have the form of the HK propagator with R_t replaced by $R_t g_t^{(n)}$. It is important to stress that the functions $g_t^{(n)}(p,q)$ are independent of $\hbar$, so that the only apparent $\hbar$ dependence in each term of (2.13), beyond that occurring in the HK approximation, arises from the factor $\hbar^n$ multiplying the $K_t^{(n)}$. This is one key feature that distinguishes the present expressions from those of Pollak and coworkers [22–26].

A general expression for the operator $\tilde{L}^{(1)}$ is given in [18]. When this is applied in (2.11) for a system with a single degree of freedom, one obtains the explicit differential equation [21]

$$\mathrm{i}\dot{g}_t^{(1)} = \left(\frac{4\gamma_2^2}{m} - V_2\right)\left(\frac{5}{8}\frac{b_t'^2}{b_t^4} - \frac{1}{4}\frac{b_t''}{b_t^3}\right) + V_3\left(\frac{5}{12}\frac{b_t'c_t}{b_t^3} - \frac{1}{6}\frac{c_t'}{b_t^2}\right) - \frac{1}{8}V_4\frac{c_t^2}{b_t^2}, \qquad (2.15)$$

for the first-order correction function $g_t^{(1)}$, where $V_n = \partial^n V(q_t)/\partial q_t^n$,

$$c_t \equiv \frac{\partial q_t}{\partial z} = \frac{1}{2}\frac{\partial q_t}{\partial p} - \frac{1}{4\mathrm{i}\gamma_1}\frac{\partial q_t}{\partial q}, \qquad (2.16)$$

and primes denote differentiation with respect to z. Formal expressions for the higher order operators $\tilde{L}^{(n)}, n > 1$ can be obtained by the procedure described in [18]. These can be reduced to computationally useful forms, allowing one to derive explicit expressions for the differential equations (2.12), for arbitrary order n, in analogy to (2.15). Since the expressions become increasingly complex with increasing n, this step is most conveniently accomplished using computer algebra.

3. Numerical application

HK and HOHK calculations of tunneling probabilities were performed for scattering in the one-dimensional Eckart system defined by the Hamiltonian [27]

$$H(p,q) = p^2/2m + V_0\,\mathrm{sech}^2(q/a). \qquad (3.1)$$

The potential energy function describes a symmetric barrier about $q = 0$ of height V_0 which decays to small values for $|q| \gg a$. The parameters were chosen as $V_0 = 0.425$ eV, $a = 0.734$ au, and $m = 1060$ au, mimicking those for the H+H_2 exchange reaction. The transmission amplitude $\mathcal{S}(E)$ at energy E can be calculated from the expression [28]

$$\mathcal{S}(E) = \lim_{x_0\to-\infty}\lim_{t\to\infty}\exp(\mathrm{i}Et/\hbar)\frac{\langle p'|\Psi_t\rangle}{\langle p'|\Psi_0\rangle}, \qquad (3.2)$$

where Ψ_t is the wave packet that evolves at time t from the initial state Ψ_0 which is localized in space about the point $x_0 < 0$ to the left of the barrier and $|p'\rangle$ is the momentum eigenfunction associated with eigenvalue

$$p' = \sqrt{2mE}. \qquad (3.3)$$

We note that, although the value of $\langle p'|\Psi_t\rangle$ depends on the function Ψ chosen, this dependence is canceled from $\mathcal{S}$ in the indicated limits by the factor $\langle p'|\Psi_0\rangle$ appearing in the denominator of (3.2).

In the present calculations we chose the initial wave packet as the coherent state wavefunction

$$\langle x|\Psi_0\rangle = \left(\frac{2\alpha}{\pi\hbar}\right)^{1/4}\mathrm{e}^{-\alpha(x-x_0)^2/\hbar + \mathrm{i}p_0(x-x_0)/\hbar} \qquad (3.4)$$

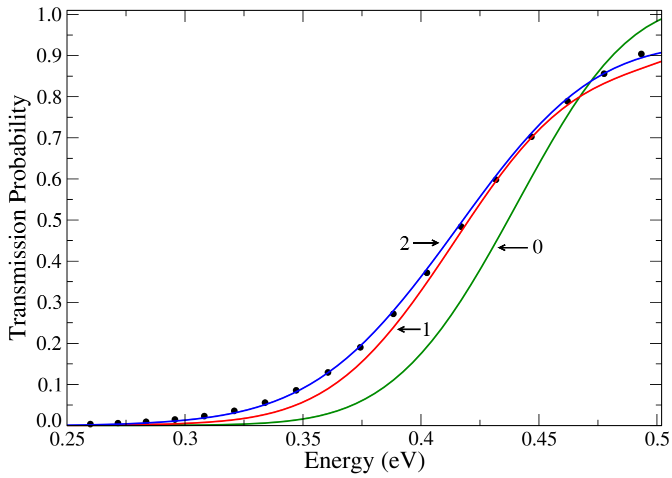

Figure 1. Transmission probabilities for the Eckart system obtained with the HOHK treatment. The curves labeled 0, 1 and 2 denote results of the zeroth, first and second-order approximations, respectively. The circles are the exact quantum results.

and determined the wavefunction at time t as

$$\langle x'|\Psi_t\rangle = \int_{-\infty}^{\infty} K_t(x', x)\langle x|\Psi_0\rangle \tag{3.5}$$

using IVR approximations for K_t. The quantities $\langle p'|\Psi_t\rangle$ at the initial and final times in (3.2) were obtained by Fourier transforming the corresponding $\langle x'|\Psi_t\rangle$. The HK and HOHK expressions allow this step to be performed analytically.

Figure 1 reports calculations of the transmission probability

$$P(E) = |\mathcal{S}(E)|^2 \tag{3.6}$$

obtained using the usual (zeroth order) HK approximation, the first-order HOHK approximation and the second-order HOHK approximation. Also shown in this figure are the quantum results obtained from an exact formula for $\mathcal{S}(E)$ [27, 29]. The IVR calculations were performed using initial wave packet parameters $p_0 = 5.7$ au, $x_0 = -10$ au and $\alpha = 1.0$ au. This state was evolved to time $t = 4000$ au using HK and HOHK propagators with Gaussian width parameters $\gamma_1 = \gamma_2 = 0.5$ au. The phase space integrations were performed by a Monte Carlo technique using 4×10^4 sample points. Calculation of the HOHK integrand for each such point requires numerical integration of a set of ordinary, time-dependent differential equations to determine the functions q_t, p_t, S_t, as well as the quantities b_t and c_t and their derivatives with respect to z, and the functions $g_t^{(n)}$ and their derivatives with respect to z (needed in calculations for orders greater than one). As the order of the approximation increases from zero to one to two, the number of *real* differential equations that must be solved per trajectory for a one-dimensional system increases from 7 to 17 to 31. The expressions to be integrated with respect to time also become more complex as the order is increased. As a result, the computational time per trajectory is about 1.8 times greater for a first-order calculation than for an ordinary zeroth-order (HK) treatment and is about 2.7 times greater for a second-order computation than for a first-order calculation.

The zeroth-order results in figure 1 resemble those obtained using a different IVR technique in [15] and are substantially inaccurate in the energy range shown. The reason for this similarity will be clarified below where we show that the two approximations are essentially equivalent for this system. Thus, as in the earlier work [15], we can attribute the inaccuracy of the present results to the existence of caustics points in the complex plane of initial conditions where the HK prefactor R_t vanishes. We will analyze this issue further in sections to follow.

Figure 1 demonstrates that the first-order and second-order corrections significantly improve the accuracy of the HK results. The third-order corrections were found to be very small so that such higher order results are not displayed. The observation that the HOHK treatment can substantially overcome the inaccuracies of the HK approximation for tunneling is one of the principal results of this work. In the remainder of this paper we attempt to understand how the semiclassical corrections operate in this case, especially in view of our previous analysis of tunneling in this system by IVR methods [15].

4. Simplification of the IVR treatments

To enable a detailed analysis of the IVR corrections for tunneling, we wish to reduce the HK and HOHK expressions to simpler forms. These steps are based on the analytical formulae for the classical quantities entering the HK propagator expression for the Eckart system. [15] For the present purposes, these exact expressions can be further simplified since the calculation of $\mathcal{S}(E)$ requires the classical variables only in the asymptotic limits $t \to \infty$ and $x_0 \to -\infty$.

It is important to note that, under these limiting conditions, the classical variables become singular functions of the initial momentum p at $p = p_s$, where

$$p_s \equiv \sqrt{2mV_0} \tag{4.1}$$

is the momentum corresponding to the barrier energy V_0. For example q_t has a logarithmic branch point and p_t has a discontinuity at $p = p_s$. Thus, the integral over all p in (2.2) naturally decomposes into an integral from $-\infty$ to p_s and an integral from p_s to ∞. It was shown in [15] that the range of integration over p in the IVR calculation of the tunneling amplitude could be restricted to $p_s < p < \infty$ so that only classical trajectories with energies greater than V_0 entered the calculation. Accurate results for $\mathcal{S}(E)$ when $E < V_0$ were nevertheless possible because the integrand could be analytically continued from the path along the real p-axis, through the complex plane, to values $p < p_s$ lying on the real axis below the singularity.

Test calculations verify that the integration over p in the HK propagator, (2.2), can also be restricted to the range $p_s < p < \infty$ for the evaluation of the tunneling probability using (3.2). Therefore, to simplify our expression for $\mathcal{S}(E)$, we focus on asymptotic formulae for the classical variables for the case $p_s < p$. For conditions

$$q \ll -a, \quad (q + pt/m) \gg a, \quad (p - p_s)/p_s \gg \exp(2q/a), \tag{4.2}$$

appropriate for application of (3.2), it is possible to derive the approximate formulae [15]

$$q_t = q + \frac{pt}{m} + a \ln\left(\frac{p^2 - p_s^2}{p^2}\right), \tag{4.3}$$

$$p_t = p, \tag{4.4}$$

and

$$S_t = \frac{p^2 t}{2m} - ap_s \ln\left(\frac{p + p_s}{p - p_s}\right), \tag{4.5}$$

from which one can also demonstrate that

$$\frac{\partial q_t}{\partial p} = \frac{t}{m} + \frac{2ap_s^2}{p\left(p^2 - p_s^2\right)}, \tag{4.6}$$

$$\frac{\partial p_t}{\partial p} = 1, \tag{4.7}$$

$$\frac{\partial q_t}{\partial q} = 1, \tag{4.8}$$

and

$$\frac{\partial p_t}{\partial q} = 0. \tag{4.9}$$

It is shown in appendix A that substitution of these expressions in (2.2) for the HK propagator allows the integral over q to be evaluated analytically. As a result, one obtains a simpler expression for K_t, (A.6), involving only a single integral. For the present conditions, this is equivalent to

$$K_t(x', x) = \left(\frac{1}{2\pi\hbar}\right)\int \mathrm{d}p\left(\frac{\partial p_t}{\partial p} - 2\mathrm{i}\gamma\frac{\partial x_t}{\partial p}\right)^{1/2} \mathrm{e}^{-\gamma(x'-x_t)^2}\,\mathrm{e}^{\mathrm{i}p_t(x'-x_t)/\hbar}\,\mathrm{e}^{\mathrm{i}S_t(p,x)/\hbar}, \tag{4.10}$$

with $\gamma = \gamma_1\gamma_2/(\gamma_1 + \gamma_2)$.

To understand how the semiclassical correction terms should be applied to this expression for K_t, we note that an alternative derivation of (4.10) from (2.2) exists. Considering the limit as $\gamma_1 \to \infty$ in equations (2.4) and (2.5), we find that

$$\lim_{\gamma_1\to\infty} R_t \exp[-\gamma_1(x-q)^2/\hbar] = \left(\frac{\partial p_t}{\partial p} - 2\mathrm{i}\gamma\frac{\partial x_t}{\partial p}\right)^{1/2}\delta(x-q) \tag{4.11}$$

with $\gamma = \gamma_2$. When substituted in (2.2), the delta function eliminates the integration over q, yielding a result identical to (4.10). Since the limit $\gamma_1 \to \infty$ converts $\partial/\partial z$ to $(1/2)\partial/\partial p$ (see (2.7)), and q_t to x_t, this derivation shows that the expression for b_t reduces to $(1/2)(\partial p_t/\partial p - 2\mathrm{i}\gamma\,\partial x_t/\partial p)$ in the present approximation for K_t. Similarly, equations (2.11) and (2.12), determining the HK correction terms $g_t^{(n)}$, remain valid in the present case with the same substitutions. This conclusion can be verified by comparison of the treatment in [18] with that of appendix D in [30]. However, since it is awkward to interpret the primes appearing in equations such as (2.15) as $(1/2)\partial/\partial p$, we find it preferable, for notational convenience, to *redefine* b_t for the IVR expression of (4.10) as

$$b_t = \frac{\partial p_t}{\partial p} - 2\mathrm{i}\gamma\frac{\partial x_t}{\partial p}. \tag{4.12}$$

This is equivalent to replacing q_t with x_t and z with p in (2.6). In this way, (2.12) for $\dot{g}_t^{(1)}$ continues to be applicable for the simplified IVR propagator if, e.g., c_t is interpreted as

$$c_t = \frac{\partial x_t}{\partial p}, \tag{4.13}$$

and the primes are now understood as denoting derivatives with respect to p, e.g., $b_t' = \partial b_t/\partial p$.

It is also shown in appendix A that substitution of (4.10) for the propagator into (3.2) leads to the formula

$$\mathcal{S}(E) = (-2\pi\mathrm{i}\hbar)^{1/2}\,\mathrm{e}^{\mathrm{i}(p'^2t/2m+p'x)/\hbar}K_t(p', x), \tag{4.14}$$

where

$$K_t(p', x) = (-2\pi\mathrm{i}\hbar)^{-1/2}\int_{-\infty}^{\infty}\mathrm{d}x'\,\mathrm{e}^{-\mathrm{i}p'x'/\hbar}K_t(x', x) \tag{4.15}$$

is the propagator in the final momentum-initial position representation, and is approximated by the IVR formula

$$K_t(p', x) = (2\pi\hbar)^{-1} \int \mathrm{d}p[\sigma_t(p)]^{1/2}\, \mathrm{e}^{-(p'-p_t)^2/(4\gamma\hbar)}\, \mathrm{e}^{-\mathrm{i}p'x_t/\hbar}\, \mathrm{e}^{\mathrm{i}S_t(p,x)/\hbar}, \tag{4.16}$$

where

$$\sigma_t(p) = \frac{\partial x_t}{\partial p} + \frac{\mathrm{i}}{2\gamma}\frac{\partial p_t}{\partial p} = \frac{\mathrm{i}}{2\gamma} b_t(p). \tag{4.17}$$

In (4.14) and in subsequent equations for $\mathcal{S}$, the limits $t \to \infty$ and $x \to -\infty$ are suppressed. Although these limits are implicit in the formal expressions, computations are carried out with large but finite values of t and $|x|$.

It is useful to note that (4.14) for $\mathcal{S}(E)$ can be obtained by an alternative method which simply involves choosing $|\Psi_0\rangle$ in (3.2) as a position eigenstate so that $\langle x|\Psi_0\rangle = \delta(x - x_0)$. [15] Equations (4.14) and (4.16) were used for the computations and analyses of tunneling in the Eckart system presented in [15]. We have now established that this simplified IVR approach is equivalent to the full HK treatment for $\mathcal{S}(E)$ described in section 3. Although we have established the relationship between these treatments only for the special case of the Eckart system, it appears possible to demonstrate that similar conclusions apply for calculations of $\mathcal{S}(E)$ in general, one-dimensional, unbound, symmetrical systems.

These developments allow us to analyze the numerical results obtained in the previous section in terms of the simpler formula

$$\mathcal{S}^{(0)}(E) = (2\pi \mathrm{i}\hbar)^{-1/2} \int_{p_s}^{\infty} \mathrm{d}p[\sigma_t(p)]^{1/2}\, \mathrm{e}^{\mathrm{i}\phi_t(p,p')/\hbar}, \tag{4.18}$$

which is obtained by substituting (4.16) into (4.14), choosing the lower integration limit as p_s, and defining

$$\phi_t(p, p') = p'^2 t/2m + \mathrm{i}(p' - p_t)^2/4\gamma + p'(x - x_t) + S_t(p, x). \tag{4.19}$$

We have added the superscript (0) to $\mathcal{S}$ to emphasize that the present expression constitutes the zeroth-order (uncorrected) IVR approximation to the scattering amplitude.

Substituting the asymptotic formulae of equations (4.3)–(4.9) in equations (4.17) and (4.19), we can derive the approximations

$$\sigma_t(p) = \beta + \frac{2ap_s^2}{p\left(p^2 - p_s^2\right)}, \tag{4.20}$$

and

$$\phi_t(p, p') = \tfrac{1}{2}\beta(p - p')^2 - a[(p' + p_s)\ln(p + p_s) + (p' - p_s)\ln(p - p_s) - 2p'\ln p], \tag{4.21}$$

where

$$\beta = \frac{t}{m} + \frac{\mathrm{i}}{2\gamma}. \tag{4.22}$$

We note that the resulting scattering amplitude $\mathcal{S}^{(0)}$ is independent of the initial position x and depends on parameters t and γ only through the variable β.

As implied by our discussion concerning (4.10), higher order approximations to $\mathcal{S}(E)$ are obtained by substituting

$$[\sigma_t(p)]^{1/2} \to [\sigma_t(p)]^{1/2} \sum_{n\geqslant 0} \hbar^n g_t^{(n)}(p) \tag{4.23}$$

in (4.18), where $g_t^{(n)}$ are obtained from equations (2.11) and (2.12) by defining b_t according to (4.12) and replacing q_t with x_t and z with p. We thus obtain the expansion

$$\mathcal{S}(E) = \sum_{n\geqslant 0} \hbar^n \mathcal{S}^{(n)}(E) \tag{4.24}$$

where

$$\mathcal{S}^{(n)}(E) = (2\pi \mathrm{i}\hbar)^{-1/2} \int_{p_s}^{\infty} \mathrm{d}p[\sigma_t(p)]^{1/2} g_t^{(n)}(p)\, \mathrm{e}^{\mathrm{i}\phi_t(p,p')/\hbar}. \tag{4.25}$$

We now attempt to simplify the first-order correction term $g_t^{(1)}$ with the objective of obtaining a more transparent formula for $\mathcal{S}^{(1)}$. An exact expression for $g_t^{(1)}$, obtained by integrating (2.15), is presented in appendix B. This result is applicable for the first-order HOHK propagator and (with the substitutions described above) for the term $\mathcal{S}^{(1)}$ in (4.24). An analogous formula has been presented by Alonso and Forbes [31, 32] in the context of electromagnetic wave propagation. We wish to simplify it for use in (4.25) for $\mathcal{S}^{(1)}(E)$ by applying the long-time asymptotic expressions for the classical variables.

To accomplish this, we substitute (4.7) in (4.12) to obtain

$$b_t = 1 - 2\mathrm{i}\gamma c_t, \tag{4.26}$$

where we have used (4.13). This allows us to apply the relation

$$\frac{1}{c_t} = 2\mathrm{i}\gamma + \frac{b_t}{c_t} \tag{4.27}$$

in (B.5), yielding

$$g_t^{(1)} = \frac{\gamma}{12}\left(\frac{3b_t''}{b_t^2} - \frac{5b_t'^2}{b_t^3}\right) + \frac{\mathrm{i}}{24}\left(\frac{5c_t'^2}{c_t^3} - \frac{3c_t''}{c_t^2}\right) + I, \tag{4.28}$$

where I is the integral over time defined in (B.6).

We can make further progress by examining the singularities in the various terms in (4.28). Although the second term in this expression is singular when $c_t = 0$, comparison with (2.15) shows that $g_t^{(1)}$ only has singularities at points (referred to later as caustics) where $b_t = 0$. Thus, the singularities at $c_t = 0$ are canceled by those in the integral I. It is therefore tempting to combine I with the second term in (4.28) to obtain a quantity that is free from such singularities. However, this second term also has singularities at $p = p_s$ since, near this point, c_t behaves as $a/(p - p_s)$ (see (4.6)) so that $c_t'^2$ and c_t'' tend to infinity more rapidly than the quantities c_t^3 and c_t^2 in the denominators. These singularities are not canceled by I but by similar singularities in the first term of (4.28). Therefore, to obtain an expression for $g_t^{(1)}$ which is free from these spurious singularities, we express I as

$$I = \frac{3\mathrm{i}c_t''}{24}\left(\frac{1}{c_t^2} - \frac{1}{\bar{c}_0^2}\right) - \frac{5\mathrm{i}c_t'^2}{24}\left(\frac{1}{c_t^3} - \frac{1}{\bar{c}_0^3}\right) + I_{ns}, \tag{4.29}$$

where

$$\bar{c}_0 \equiv \frac{a}{p - p_s}, \tag{4.30}$$

and I_{ns} is implicitly defined by this equation. The quantities involving negative powers of $\bar{c}_0$ cancel the singularities at $p = p_s$ so that the first two terms of (4.29) contain the singularities in I at $c_t = 0$ and the remainder term I_{ns} is nonsingular by construction. Substitution in (4.28) then gives

$$g_t^{(1)} = \frac{3\gamma b_t''}{12}\left(\frac{1}{b_t^2} - \frac{1}{\bar{b}_0^2}\right) - \frac{5\gamma b_t'^2}{12}\left(\frac{1}{b_t^3} - \frac{1}{\bar{b}_0^3}\right) + I_{ns} \tag{4.31}$$

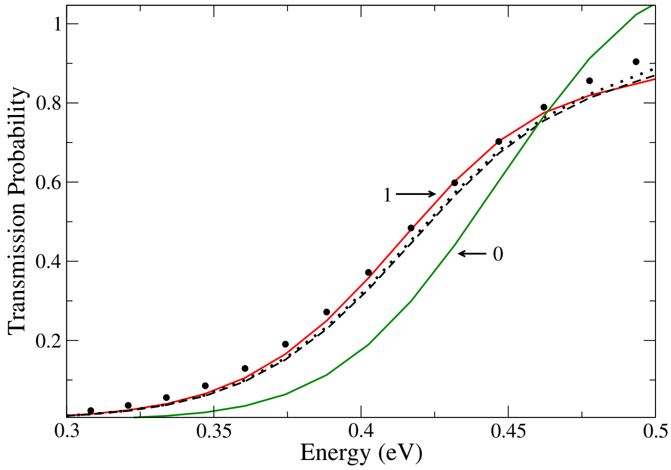

Figure 2. Transmission probabilities for the Eckart system obtained with the IVR treatment of (4.24). The curve labeled 0 is the zeroth-order approximation and the curve labeled 1 is the first-order approximation with the integral I of (4.28) calculated numerically. The dashed and dotted curves are first-order results obtained using (4.31) with $I_{ns} = 0$ and (6.15) with $I_{ns} = 0$, respectively. The exact quantum results are shown as circles.

where

$$\bar{b}_0 \equiv -2\mathrm{i}\gamma\bar{c}_0 = -\frac{2\mathrm{i}\gamma a}{p - p_s}. \tag{4.32}$$

Examination of (4.31) near $p = p_s$ shows that the factors $\left(b_t^{-k} - \bar{b}_0^{-k}\right)$ cancel the singularities occurring in the factors b_t'' and $b_t'^2$ at $p = p_s$. In this way, we obtain a simpler formula for $g_t^{(1)}$ in which all singular terms are displayed explicitly.

Figure 2 reports calculations of the transmission probabilities for the Eckart system based on the zeroth-order IVR treatment ($P = |\mathcal{S}^{(0)}|^2$) and the first-order corrected IVR approximation ($P = |\mathcal{S}^{(0)} + \hbar\mathcal{S}^{(1)}|^2$) with $g_t^{(1)}$ calculated using (B.5) and the integral I evaluated numerically using the trapezoid rule with 1000 points. The parameters are chosen to be $\gamma = 1.0$ au and $t = 5300$ au, and the details for computation of the integral over p are similar to those described in [15]. The results of these calculations resemble those shown in figure 1: the zeroth-order probability is substantially inaccurate but the first-order probability is in much better agreement with the exact quantum results. The figure also reports an approximate calculation of the first-order probability using (4.31) for $g_t^{(1)}$ with the remainder term I_{ns} neglected. Although differences from the more exact first-order probability are visible, the effects of I_{ns} are found to be small and the results are still in good qualitative agreement with the quantum probabilities. Similar conclusions have been verified for other values of γ.

The neglect of I_{ns} allows very efficient calculations of the first-order corrected tunneling probabilities. In figure 3 such calculations are reported on a semilogarithmic scale for $\gamma = 0.5$ and $\gamma = 10.0$. As the energy approaches $V_0 = 0.425$ au from below, the first-order curves for both values of γ become indistinguishable and provide significant improvements to the zero-order approximation. For lower energies, however, the two curves diverge from one another; the curve for $\gamma = 0.5$ becomes inaccurate while the that for $\gamma = 10.0$ appears to remain surprisingly accurate even for energies close to zero.

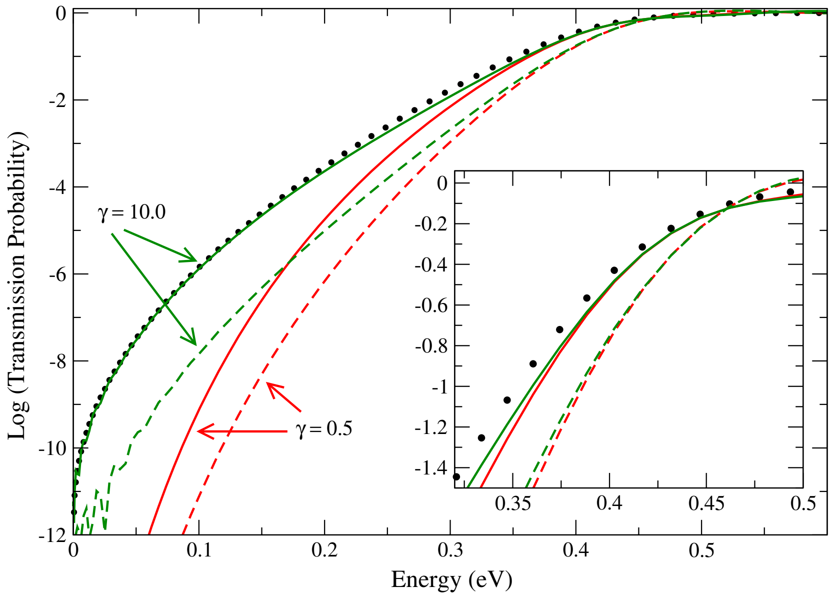

Figure 3. Transmission probabilities for the Eckart system obtained with the IVR treatment of (4.24) using two different values of γ. The dashed curves are zeroth-order results approximation and the solid curves are first-order results obtained using (4.31) with $I_{ns} = 0$. The exact quantum results are shown as circles. The inset shows a close-up for energies near the barrier height.

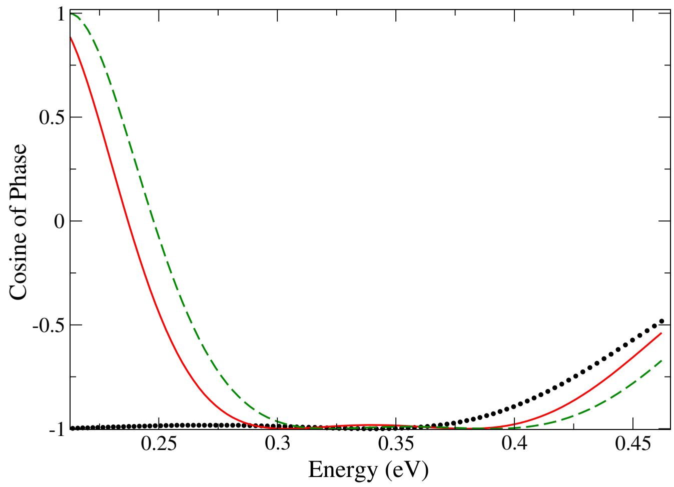

Figure 4. The function $\cos[\arg(\mathcal{S}(E))]$. Dashed curve: zeroth-order IVR approximation; solid curve: first-order approximation; dots: exact quantum result.

Since this last behavior was an obstacle to understanding the nature of the corrections, we emphasize that the accuracy seen in figure 3 for $\gamma = 10.0$ and low energies is misleading. The transmission probabilities that are displayed depend only on the modulus of $\mathcal{S}$, not on its phase. To examine this latter property, figure 4 examines the quantity $\cos[\arg(\mathcal{S})]$ obtained for $\gamma = 10.0$ using the zeroth- and first-order approximations (the results for $\gamma = 0.5$ are very similar and are not displayed). For energies in the range from 0.30 to 0.37 eV, both the zeroth-order and first-order approximations for the phase are seen to be excellent. For energies above this range, the accuracy of these approximations is poorer, but the difference between the exact and semiclassical phases is still not large and the first-order approximation provides a modest improvement in accuracy. For energies below about 0.26 eV, however, both the zeroth- and first-order approximations become very inaccurate. Thus, the apparent success of the first-order approximation for the probabilities in this case does not imply similar accuracy for the corresponding $\mathcal{S}(E)$ at low energies. Indeed, further calculations show that the accuracy of the first-order probabilities decreases at low energies if γ is chosen to be much larger than 10. Thus, the low energy accuracy for $\gamma = 10.0$ in figure 3 appears to be fortuitous and the range of good agreement between the first-order and exact quantum results is restricted to energies greater than or about equal to 0.3 eV for both values of γ investigated here.

5. The issues

The ability of the SC corrections to improve the description of tunneling, observed in the previous sections, raises a number of questions. To bring these issues into focus, we briefly review the conditions that enable the zeroth-order IVR approximation of (4.18) to describe tunneling semiclassically.

Previous analysis [15] concerning the validity of the IVR approximation for tunneling was based on the observation that the treatment will be accurate if the method of steepest descents can be applied to the integral over p in (4.18) to yield the primitive semiclassical (PSC) result [33]

$$\mathcal{S}_{psc}(E) = \exp(\mathrm{i}\phi_r/\hbar), \tag{5.1}$$

which becomes exact as $\hbar \to 0$ (the error in the approximation is of order $\hbar \exp(\mathrm{i}\phi_r/\hbar)$). The function ϕ_r appearing here is defined as

$$\phi_r \equiv \phi_t(p', p'). \tag{5.2}$$

This, condition will be obeyed if (a) the complex phase function $\phi_t(p, p')$ has a saddle point (where $\partial\phi_t/\partial p = 0$) at $p = p'$, (b) the integration path along the real axis can be deformed to the path of steepest descent (SD) from this point and (c) $\partial^2\phi_t/\partial p^2 = \sigma_t$ at $p = p'$. This last condition is needed in order for the pre-exponential factor arising from the SD treatment to cancel the factor $\sigma_t^{1/2}(p')/(2\pi \mathrm{i}\hbar)^{1/2}$ in the integrand of (4.18) at $p = p'$, to produce the coefficient 1 for the exponential in (5.1).

To locate the saddle points for the analytically continued integrand, we note that differentiation of (4.19) and application of (4.17) gives

$$\frac{\partial\phi_t(p, p')}{\partial p} = -\sigma_t(p)(p' - p). \tag{5.3}$$

Thus, $\phi_t(p, p')$ indeed has a saddle point at $p = p'$ where $\phi_t = \phi_r$, as needed. Additionally, we note that $\partial^2\phi_t/\partial p^2 = \sigma_t(p')$ at $p = p'$, as required. We refer to this saddle point as the *root*. Provided that the integration path can be deformed through this point, an SD treatment indeed gives the correct PSC result, (5.1), and the zeroth-order IVR treatment for tunneling is accurate.

However (5.3) shows that ϕ_t can also have saddle points for certain values of p, denoted as $p = p_c$, where $\sigma_t(p_c) = 0$. These points are referred to as *caustics*. If the integration path in (4.18) is deformable to the SD contour that passes through such a caustic, instead of the one through the root, one obtains an asymptotic result for $\mathcal{S}$ in the $\hbar \to 0$ limit which involves the factor $\exp(\mathrm{i}\phi_c/\hbar)$, where

$$\phi_c \equiv \phi_t(p_c, p'). \tag{5.4}$$

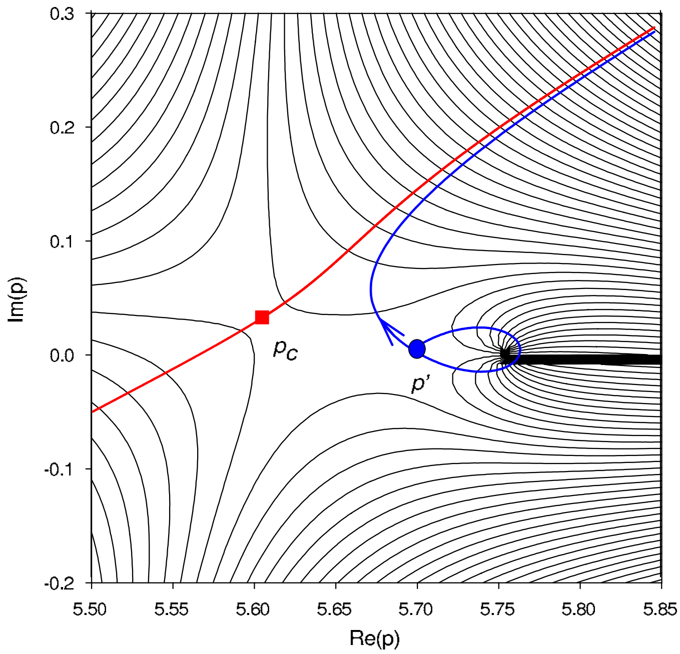

Figure 5. Contour plot of $\text{Im}\phi_t(p, p')$ for $p' = 5.70$ and $\gamma = 0.5$. Paths of steepest descent from the saddle points at p' and p_c are shown. The heavy line extending rightwards from $p_s \approx 5.754$ is a branch cut that coincides with the real integration path. In the present case, this path can be deformed to the steepest descent path through the root at $p = p'$.

This result is semiclassically incorrect since, in general, p_c is unrelated to p' so that $\phi_c \neq \phi_r$. Thus, the zeroth-order IVR treatment of tunneling is inaccurate in this case.

These considerations show that the accuracy of the zeroth-order IVR description of tunneling depends on the ability to deform the real integration path to an SD contour passing through the root rather than a caustic. This, in turn, depends on the relative dispositions of points p' and p_c in the complex plane. Consider the case in which, roughly speaking, the lower integration limit p_s, in equation (4.18), is closer to the root p' than the nearest caustic p_c. Figure 5 shows contours for the function $\text{Im}\phi_t(p, p')$, obtained for the choices $p' = 5.70$ and $\gamma = 0.5$, which illustrate this situation. Shown are two, partially overlapping saddles, one at the root and one at a nearby caustic where $p_c \approx 5.61 + 0.03\text{i}$. Also displayed are SD paths through each saddle. The real integration path from $p = p_s \approx 5.754$ to ∞ coincides with a logarithmic branch cut of ϕ_t and the IVR integrand vanishes in the upper right half-plane. The looped portion of the SD path through the root is discussed thoroughly in [15]. It is sufficient to note here that the loop can be shrunken to the point p_s so that the lower limit of the path through the root can be taken as p_s and this path can be deformed to the real integration path.

Thus, in the case illustrated by this figure, the IVR treatment asymptotically gives the correct PSC result of (5.1). The corresponding expression for the tunneling probability has a particularly simple form. The quantity $p - p_s$ appearing in (4.21) has the value $(p_s - p')\,\text{e}^{\text{i}\pi}$ when it is analytically continued to the root along the SD path, so that $\text{Im}\,\phi_r = \pi a(p_s - p')$ and one obtains

$$P_{psc}(E) \equiv |\mathcal{S}(E)|^2 = \exp[-2\pi a(p_s - p')/\hbar]. \tag{5.5}$$

These PSC probabilities become inaccurate when $2\pi a|p' - p_s|/\hbar$ is small because the proximity of the saddle point to the branch point at p_s makes the simplest stationary phase

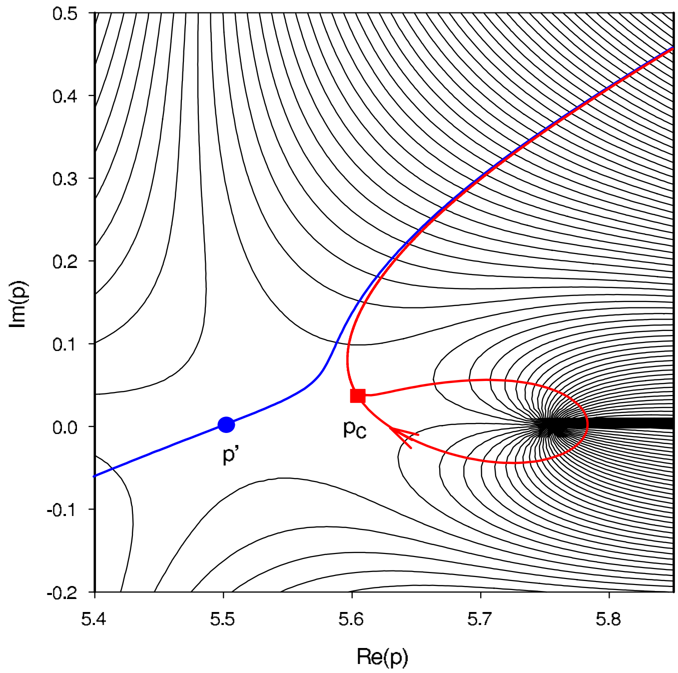

Figure 6. Contour plot of Im$\phi_t(p, p')$ for $p' = 5.50$ and $\gamma = 0.5$. Paths of steepest descent from the saddle points at p' and p_c are shown. The heavy line extending rightwards from $p_s \approx 5.754$ is a branch cut that coincides with the real integration path. In the present case, this path can be deformed to the steepest descent path through the caustic at $p = p_c$.

treatment invalid. However, in this case, it can be shown [15] that the IVR expression actually approximates the more accurate uniform semiclassical result for the tunneling probability

$$P_{usc}(E) = \frac{1}{1 + \exp[2\pi a(p_s - p')/\hbar]}. \tag{5.6}$$

The conclusion is that, when the real integration path can be deformed to the SD path through the root, the uncorrected IVR treatment of (4.18) already describes tunneling with real trajectories as $\hbar \to 0$, and yields good accuracy for small-to-moderate values of $\hbar$. It is, therefore, reasonable to expect that this result can be further improved in such cases by adding corrections proportional to various powers of $\hbar$, as in (4.25). The overall situation is similar to that which is expected for the application of the semiclassical IVR corrections to classically allowed dynamics. Thus, the ability of the corrections to improve the accuracy of the ordinary IVR treatment does not seem to be surprising or to introduce significant new issues in this case.

Now, however, we turn attention to the case where, roughly speaking, p_s is closer to p_c than p'. Figure 6 shows contours for the function Im $\phi_t(p, p')$, for $p' = 5.50$ and $\gamma = 0.5$, illustrating this situation. We again see overlapping saddles at $p = p_c$ and $p = p'$ and the SD paths through these points. However, the roles of the two saddles have switched from the case considered in the previous figure. Here, it is the path through the saddle at p_c that can be deformed to the real integration path from p_s to ∞. Thus, an SD treatment establishes that the IVR expression for $\mathcal{S}(E)$ is asymptotically proportional to $\exp(i\phi_c/\hbar)$ as $\hbar \to 0$. The validity of this conclusion was confirmed numerically in [15]. Thus, in this case, the SD treatment does not yield the correct classically limiting formula for the tunneling amplitude and a zero-order IVR calculation of this property yields inaccurate results.

Although our treatment will be valid under somewhat more general circumstances (see section 7), we focus on this latter case since it is less obvious how the corrections operate to improve the accuracy of the tunneling calculation. Indeed, since the zeroth-order term in the $\hbar$ expansion of (4.24) is not correct as $\hbar \to 0$, it would seem impossible to correct it by adding terms proportional to positive powers of $\hbar$ which should vanish as $\hbar \to 0$.

An additional basic problem can be identified for this case. Since $g_t^{(n)}$ are independent of $\hbar$, the only $\hbar$-dependence of each term $\mathcal{S}^{(n)}$ in (4.24) is due to the same rapidly varying factor $\exp(\mathrm{i}\phi_t/\hbar)$. It should, therefore, be possible to estimate each integral $\mathcal{S}^{(n)}$ in the limit $\hbar \to 0$ by the same SD treatment used for the zero-order term. This would imply that each term in the expansion has the form

$$\hbar^n \mathcal{S}_n(E) \approx \hbar^n A_n(E, \hbar) \exp(\mathrm{i}\phi_c/\hbar), \tag{5.7}$$

involving the same factor $\exp(\mathrm{i}\phi_c/\hbar)$ and various coefficients A_n. Consequently, the asymptotic formula for $\mathcal{S}(E)$, to arbitrary order in $\hbar$, should be expressible as $\exp(\mathrm{i}\phi_c/\hbar)$ multiplied by a series in $\hbar$. Even allowing for the possibility that the A_n can be expanded in powers of $\hbar$, we face a basic difficulty: the correct result for $\mathcal{S}(E)$ as $\hbar \to 0$, namely $\exp(\mathrm{i}\phi_r/\hbar)$, has an essential singularity at $\hbar = 0$. Thus, it cannot generally be expanded in powers of $\hbar$ about the function $\exp(\mathrm{i}\phi_c/\hbar)$ in the limit as $\hbar \to 0$.

At issue is the nature of the correction expansion in the present case. The questions we wish to address include: how does the treatment improve the accuracy of the zero-order IVR results? Under what conditions is it applicable? Is the expansion capable of describing the semiclassical limit?

6. Analysis

6.1. Strategy

The problems concerning the essential singularity at $\hbar = 0$, described above, can be circumvented by confining the energy range for the applicability of the correction treatment to values corresponding to momenta p' in the vicinity of the caustic p_c nearest p_s. In particular, although the quantity

$$\delta \equiv p_c - p' \tag{6.1}$$

is ostensibly 'classical' and independent of $\hbar$, we propose restricting the values of p' in the present treatment so that δ scales as $\hbar^{1/3}$ in the classical limit. Since p_c is close to p_s in the cases considered (see (6.12) below), this scaling assumption effectively confines the range of applicability of the corrected IVR treatment to cases where $p_s - p'$ is small so that the energies are not too far below the barrier. This restriction appears consistent with the range of accuracy for the first-order tunneling amplitudes observed in section 4. However, even for this range of energies, the tunneling probabilities still tend to zero as $\hbar \to 0$, so that this condition does not limit applicability of the treatment to uninteresting cases where the degree of tunneling is very small. This becomes apparent if we express P_{psc} in (5.5) as $\exp[-2\pi a(\epsilon + \delta)/\hbar]$, where

$$\epsilon \equiv p_s - p_c \tag{6.2}$$

is independent of $\hbar$. Clearly, P_{psc} vanishes as $\hbar \to 0$ even if δ is taken to scale as $\hbar^{1/3}$.

To see how this assumption eliminates the problem of the expansion of $\exp(\mathrm{i}\phi_r/\hbar)$ about $\exp(\mathrm{i}\phi_c/\hbar)$, we recall the definitions of ϕ_r and ϕ_c (equations (5.2) and (5.4)), and expand ϕ_r in a Taylor series as

$$\phi_r = \phi_c - \phi_c'\delta + \tfrac{1}{2}\phi_c''\delta^2 - \tfrac{1}{6}\phi_c'''\delta^3 + \cdots \tag{6.3}$$

where the primes denote derivatives with respect to p, as usual. Due to the logarithmic singularity in ϕ_t at $p = p_s$ (see (4.21)) the validity of this expansion is restricted to the range $|\delta| < |\epsilon|$. From (5.3) we have that

$$\phi_c' = \sigma_c \delta = 0 \tag{6.4}$$

since $\sigma_c \equiv \sigma_t(p_c) = 0$ from the definition of p_c. Differentiating both sides of (5.3) with respect to p at $p = p_c$ further gives

$$\phi_c'' = \delta\sigma_c', \qquad \phi_c''' = 2\sigma_c' + \delta\sigma_c'', \qquad \phi_c^{iv} = 3\sigma_c'' + \delta\sigma_c''', \tag{6.5}$$

so that (6.3) becomes

$$\phi_r = \phi_c + \tfrac{1}{6}\sigma_c'\delta^3 + O(\delta^4), \tag{6.6}$$

so that we can write

$$\exp(\mathrm{i}\phi_r/\hbar) = A\exp(\mathrm{i}\phi_c/\hbar), \tag{6.7}$$

where

$$A = \exp\{(\mathrm{i}\sigma_c'/6)[\delta^3 + O(\delta^4)]/\hbar\}. \tag{6.8}$$

Because of the assumed scaling of δ, A can be expanded in a power series in $\hbar^{1/3}$ and the issue of the essential singularity in $\exp(\mathrm{i}\phi_r/\hbar)$ at $\hbar = 0$ does not arise.

6.2. *Further approximations for the first-order correction*

To proceed, we need to further simplify (4.31) for $g_t^{(1)}$. In view of our comments in section 5, we anticipate that, for the case exemplified by figure 6, an asymptotic $\hbar \to 0$ expression for $\mathcal{S}(E)$ can be obtained by approximating the integrals in (4.25) with a stationary phase treatment about the caustic saddle point nearest to p_s. It is, thus, in the vicinity of this caustic that we need to simplify $g_t^{(1)}$. To obtain an estimate for the position of this caustic, we note that, for small $|p - p_s|$, (4.20) yields

$$\sigma_t \approx \beta + a/(p - p_s) \tag{6.9}$$

so that

$$b_t = -2\mathrm{i}\gamma\sigma_t \approx -\left(\frac{2\mathrm{i}\gamma\beta}{p - p_s}\right)(p - p_s + a/\beta). \tag{6.10}$$

This result shows that σ_t and b_t vanish at

$$p = p_s - a/\beta, \tag{6.11}$$

which provides an approximate expression for the caustic position p_c. Comparison with (6.2) shows that

$$\epsilon \approx a/\beta = \frac{a}{t/m + \mathrm{i}/(2\gamma)}, \tag{6.12}$$

where we have applied (4.22). This shows that, for the case of large t of interest here, $|\epsilon|$ is small so that p_c is indeed close to p_s, consistent with the approximation in (6.9). Substituting (6.12) in (6.10) now yields

$$b_t \approx -\frac{2\mathrm{i}\gamma a}{\epsilon}\left(\frac{p - p_c}{p - p_s}\right). \tag{6.13}$$

Additionally, differentiating this equation with respect to p gives

$$b_t' \approx \frac{2\mathrm{i}\gamma a}{(p - p_s)^2}, \qquad b_t'' \approx -\frac{4\mathrm{i}\gamma a}{(p - p_s)^3}. \tag{6.14}$$

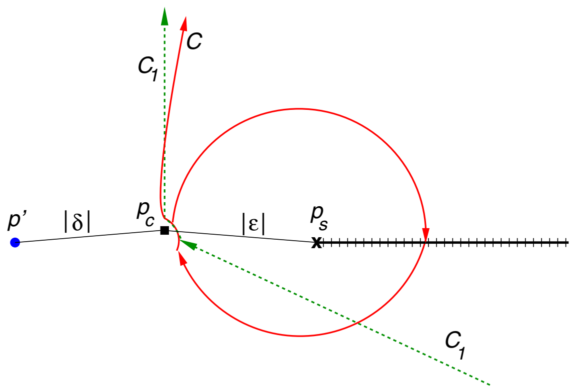

Figure 7. Schematic diagram of the integration contours C (solid) and C_1 (dashed) used to define the integrals in (6.20) and (6.33). Both curves pass slightly to the right of the caustic at $p = p_c$. The cross-hatched line denotes a logarithmic branch cut in the function $\phi_t(p, p')$.

When these results are substituted in (4.31) we obtain the very simple approximation

$$g_t^{(1)} = \frac{\mathrm{i}}{24a}\left[\frac{5\epsilon^2}{(p-p_c)^3} - \frac{\epsilon}{(p-p_c)^2} - \frac{1}{p-p_c}\right] + I_{ns}, \tag{6.15}$$

which is valid for p near p_c.

Denoting the first-order corrected expression for $\mathcal{S}(E)$ as

$$\mathcal{S}_1(E) \equiv \mathcal{S}^{(0)}(E) + \hbar\mathcal{S}^{(1)}(E), \tag{6.16}$$

and applying the above approximation for $g_t^{(1)}$, we find that we can express $\mathcal{S}_1$ as

$$\mathcal{S}_1(E) = J_0 + \frac{\mathrm{i}\hbar}{24a}(5\epsilon^2 J_3 - \epsilon J_2 - J_1) + \hbar J_{ns}, \tag{6.17}$$

in terms of the integrals

$$J_n(p') \equiv (2\pi\mathrm{i}\hbar)^{-1/2}\int_{p_s}^{\infty} \mathrm{d}p[\sigma_t(p)]^{1/2}(p-p_c)^{-n}\exp[\mathrm{i}\phi_t(p,p')/\hbar], \tag{6.18}$$

and

$$J_{ns}(p') \equiv (2\pi\mathrm{i}\hbar)^{-1/2}\int_{p_s}^{\infty} \mathrm{d}p[\sigma_t(p)]^{1/2} I_{ns}\exp[\mathrm{i}\phi_t(p,p')/\hbar]. \tag{6.19}$$

A calculation of $\mathcal{S}_1(E)$ based on (6.17) with $J_{ns} = 0$ is presented in figure 2. The results verify that the approximations leading from (4.31) to (6.15) are accurate for the range of energies of interest.

6.3. Saddle-point treatment of integrals J_n

We wish to obtain asymptotic estimates of the integrals J_n for small $\hbar$ by applying an SD treatment about the saddle at $p = p_c$ for cases similar to the one shown in figure 6. Due to the infinite singularity in (6.18) at $p = p_c$, however, it is not possible to deform the integration path for J_n so that it completely coincides with this SD contour when $n > 1$. Instead, we choose a path that resembles the SD contour but avoids the point p_c by passing slightly to its right. Such an integration contour, denoted by C, is illustrated in figure 7. We thus express J_n as

$$J_n = (2\pi\mathrm{i}\hbar)^{-1/2}\int_C \mathrm{d}u\,\sigma_t^{1/2}u^{-n}\exp[\mathrm{i}\phi_t/\hbar], \tag{6.20}$$

where $u = p - p_c$. We now expand ϕ_t and $\sigma_t^{1/2}$ in powers of u

$$\phi_t(p, p') = \phi_c + u\phi_c' + (1/2)u^2\phi_c'' + (1/6)u^3\phi_c''' + (1/24)u^4\phi_c^{iv}\cdots, \tag{6.21}$$

$$\sigma_t^{1/2}(p) = (\sigma_c')^{1/2}u^{1/2}\left(1 + \frac{\sigma_c''}{4\sigma_c'}u + \cdots\right), \tag{6.22}$$

and apply (6.4) and (6.5) to obtain

$$J_n = (2\pi \mathrm{i}\hbar)^{-1/2}(\sigma_c')^{1/2}\,\mathrm{e}^{\mathrm{i}\phi_c/\hbar}\int_C \mathrm{d}u\, u^{1/2-n}\left(1 + \frac{\sigma_c''}{4\sigma_c'}u + \cdots\right)$$
$$\times \exp\{(\mathrm{i}/\hbar)[\sigma_c'\delta u^2/2 + (2\sigma_c' + \sigma_c''\delta)u^3/6 + (3\sigma_c'' + \sigma_c'''\delta)u^4/24 + \cdots]\}. \tag{6.23}$$

The various derivatives of σ_c can be approximated by differentiating (6.9) at $p = p_c$. This gives the formula

$$\mathrm{d}^k\sigma_c/\mathrm{d}p^k = -k!a/\epsilon^{k+1}, \qquad k = 1, 2, \ldots. \tag{6.24}$$

Substituting these expressions and changing the integration variable to

$$v = \left[-\frac{(2\sigma_c' + \sigma_c''\delta)}{6\hbar}\right]^{1/3} u, \tag{6.25}$$

we can write J_n as

$$J_n = \left[-\frac{3\epsilon}{2\pi \mathrm{i}(\epsilon + \delta)}\right]^{1/2} \mathrm{e}^{\mathrm{i}\phi_c/\hbar}(\xi\epsilon)^{-n}\int_C \mathrm{d}v\, v^{1/2-n}\,\mathrm{e}^{-\mathrm{i}v^3} f(v), \tag{6.26}$$

where

$$f(v) = \exp(-3\mathrm{i}\eta v^2/2)(1 + \xi v/2 + \cdots)\exp(-3\mathrm{i}\xi v^4/4 + \cdots) \tag{6.27}$$

and where we have introduced the dimensionless variables

$$\xi = \left[\frac{3\hbar}{a(\epsilon + \delta)}\right]^{1/3}, \tag{6.28}$$

and

$$\eta = \left[\frac{a\delta^3}{3\hbar(\epsilon + \delta)^2}\right]^{1/3}. \tag{6.29}$$

Note that $\xi = O(\hbar^{1/3})$, and $\eta = O(\hbar^0)$.

For small $\hbar$ (or ξ), $f(v)$ behaves roughly like $\exp(-3\mathrm{i}\eta v^2/2)$ and the factor $\exp(-\mathrm{i}v^3)$ in J_n determines the asymptotic behavior of the integrand for $|v| \to \infty$. We may thus replace the contour C in (6.26) with a new path C_1 that originates at $\infty\mathrm{e}^{-\mathrm{i}\pi/6}$ (where $\exp(-\mathrm{i}v^3) = 0$), passes around the singularity at $v = 0$, and ends at $\infty\,\mathrm{e}^{\mathrm{i}\pi/2}$ (where again $\exp(-\mathrm{i}v^3) = 0$). Such a path is illustrated in figure 7. Having made this replacement, we expand $f(v)$ about $v = 0$ as

$$f(v) = \sum_{j=0}^{\infty} c_j v^j, \tag{6.30}$$

where, for example,

$$c_0 = 1, \qquad c_1 = \xi/2, \qquad c_2 = 3(\xi^2/8 - \mathrm{i}\eta/2), \qquad c_4 = -3\mathrm{i}\xi/4 + O(\eta^2) + O(\xi^4). \tag{6.31}$$

Other coefficients c_j contain only terms that are $O(\xi^l\eta^m)$ with $l+m>1$. While it may not be strictly necessary to include the factor $\exp(-3\mathrm{i}\eta v^2/2)$ in this expansion, doing so has the advantage of leading to expressions in terms of elementary functions. We thus obtain

$$J_n = \left[-\frac{3\epsilon}{2\pi\mathrm{i}(\epsilon+\delta)}\right]^{1/2} \mathrm{e}^{\mathrm{i}\phi_c/\hbar}(\xi\epsilon)^{-n}\sum_{j=0}^{\infty} c_j I_{n-j}, \tag{6.32}$$

where we have defined

$$I_m = \int_{C_1} \mathrm{d}v\, v^{1/2-m}\,\mathrm{e}^{-\mathrm{i}v^3}. \tag{6.33}$$

To evaluate I_m, we first consider the case $m \leqslant 1$, so that there is no problem letting the contour C_1 actually pass through the point $v=0$, corresponding to $p=p_c$. This allows us to express the integration path in terms of two straight line segments and we obtain

$$\begin{aligned} I_m &= \int_{\infty\mathrm{e}^{-\mathrm{i}\pi/6}}^{0} \mathrm{d}v\, v^{1/2-m}\,\mathrm{e}^{-\mathrm{i}v^3} + \int_0^{\infty\mathrm{e}^{\mathrm{i}\pi/2}} \mathrm{d}v\, v^{1/2-m}\,\mathrm{e}^{-\mathrm{i}v^3} \\ &= [-\mathrm{e}^{-\mathrm{i}(\pi/6)(3/2-m)} + \mathrm{e}^{\mathrm{i}(\pi/2)(3/2-m)}]\int_0^{\infty} \mathrm{d}r\, r^{1/2-m}\,\mathrm{e}^{-r^3}, \end{aligned} \tag{6.34}$$

where we have let $v = r\exp(\mathrm{i}\theta)$, with $\theta = -\mathrm{i}\pi/6$ or $\mathrm{i}\pi/2$. Finally, changing the integration variable to r^3, we can show that

$$I_m = (2\mathrm{i}/3)\,\mathrm{e}^{\mathrm{i}\pi/4-\mathrm{i}\pi m/6}\cos(\pi m/3)\Gamma(1/2-m/3). \tag{6.35}$$

Although derived for the case $m \leqslant 1$, (6.35) is actually valid for arbitrary integer m. This can be seen by integrating (6.33) by parts k times which yields

$$I_m = i^k\frac{\Gamma(1/2-m/3)}{\Gamma(1/2-m/3+k)} I_{m-3k}. \tag{6.36}$$

For sufficiently large k, $m-3k$ will be $\leqslant 1$. Substituting (6.35) with m replaced by $m-3k$ in (6.36), again yields (6.35).

Our final general expression for J_n is obtained by substituting (6.35) in (6.32), yielding

$$J_n = \left[\frac{2\epsilon}{3\pi(\delta+\epsilon)}\right]^{1/2} \mathrm{e}^{\mathrm{i}\phi_c/\hbar}(\xi\epsilon)^{-n}\sum_{j=0}^{\infty} c_j\,\mathrm{e}^{\mathrm{i}\pi(j-n)/6}\cos[\pi(j-n)/3]\Gamma[1/2+(j-n)/3]. \tag{6.37}$$

Note that each J_n is found to contain a factor $\xi^{-n} \propto \hbar^{-n/3}$. This is multiplied by a sum involving coefficients c_j proportional to powers of ξ and η corresponding to all positive orders of $\hbar^{1/3}$.

6.4. *First-order expression for $\mathcal{S}(E)$*

Applying (6.37), and keeping only terms that are, at most, of first order in ξ and η, we find the quantities needed to form $\mathcal{S}_1$ in (6.17) to be

$$\begin{aligned} J_0 \approx \left(\frac{2}{3\pi}\right)^{1/2} &\mathrm{e}^{\mathrm{i}\phi_c/\hbar}[\Gamma(1/2) - (\xi/8)\,\mathrm{e}^{\mathrm{i}\pi/6}\cos(\pi/3)\Gamma(5/6) \\ &-(3\mathrm{i}\eta/2)\,\mathrm{e}^{\mathrm{i}\pi/3}\cos(2\pi/3)\Gamma(7/6)] \end{aligned} \tag{6.38}$$

and

$$\begin{aligned} (\hbar\epsilon^{n-1}/a)J_n \approx \left(\frac{2}{3\pi}\right)^{1/2} &\mathrm{e}^{\mathrm{i}\phi_c/\hbar}(\xi^{3-n}/3)\,\mathrm{e}^{-\mathrm{i}\pi n/6}\{\cos(\pi n/3)\Gamma(1/2-n/3) \\ &-(\xi/8)\,\mathrm{e}^{\mathrm{i}\pi/6}\cos[\pi(n-1)/3](1-2n)\Gamma(5/6-n/3) \\ &-(3\mathrm{i}\eta/2)\,\mathrm{e}^{\mathrm{i}\pi/3}\cos[\pi(n-2)/3]\Gamma(7/6-n/3)\} \end{aligned} \tag{6.39}$$

For $n = 1, 2, 3$, this last expression involves non-negative powers of $\hbar$ only. In fact, the $\hbar$-dependence for $(\hbar\epsilon^2/a)J_3$ is identical to that for J_0 and both contribute terms that are $O(\hbar^0)$ to $\mathcal{S}_1$. When these formulae are substituted into (6.17) we obtain the following approximate result for $\mathcal{S}_1(E)$, valid to first order in ξ and η:

$$\mathcal{S}_1(E) \approx \mathrm{e}^{\mathrm{i}\phi_c/\hbar}\left(\frac{2}{3\pi}\right)^{1/2}\left[\pi^{1/2}\left\{\frac{41}{36}\right\} + (\xi/4)\,\mathrm{e}^{\mathrm{i}\pi/6}\Gamma(5/6)\left\{\frac{5}{48}\right\} + (3\mathrm{i}\eta/4)\,\mathrm{e}^{\mathrm{i}\pi/3}\Gamma(7/6)\left\{\frac{7}{12}\right\}\right]. \tag{6.40}$$

The analogous result for the zeroth-order IVR amplitude, $\mathcal{S}^{(0)} = J_0$, has a similar form except that the factors in the braces are replaced by unity. We are, therefore, in a position to compare the zeroth- and first-order approximations to $\mathcal{S}$. The term that is independent of ξ and η has the approximate numerical value of approximately $0.84\exp(\mathrm{i}\phi_c/\hbar)$ in the expression for $\mathcal{S}^{(0)}$. Since, $\phi_c = \phi_r$ to this order in ξ and η, this result is not far from the PSC formula of (5.1). Nevertheless, it is not identical to the PSC result, even for $\eta = 0$, corresponding to $p' = p_c$, which verifies our claims that the lowest IVR treatment does not yield the correct classical limit. Multiplication by the factor $41/36$ in $\mathcal{S}_1$ improves the approximation to about $0.93\exp(\mathrm{i}\phi_c/\hbar)$. To examine the effect of the term proportional to ξ, consider the case $\gamma = 1.0$ au, $t = 5300$ au and $\delta = 0$. Then $\xi \approx 3.04$ and the ratio of the second term to the first term in (6.40) has the magnitude 0.33 in $\mathcal{S}^{(0)}$ but only 0.03 in $\mathcal{S}_1$. Since the corresponding PSC value is zero, we see that the first-order correction is very effective in decreasing this source of error in the treatment of tunneling. To examine the term proportional to η, we assume the same values for t and γ described above but take $\delta = \epsilon$. Then $\eta = 0.33$ and the ratio of the third term to the first term in (6.40) has the magnitude 0.130 for the zeroth-order approximation and 0.067 for the first-order treatment. The semiclassically correct value should again be zero so that the first-order correction again improves the zero-order estimate.

This analysis suggests a justification for neglecting the contribution of $\hbar I_{ns}$ to $\mathcal{S}_1(E)$ in approximate calculations, such as those of section 4. Since I_{ns} is nonsingular at the caustic saddle point ($p = p_c$), the quantity $\hbar J_{ns}$ may be expected to have a smaller value than the remaining terms $\hbar J_n$, ($n = 1, 2, 3$) contributing to $\hbar\mathcal{S}^{(1)}$, which have integrands that diverge at this point. The effects of this singular behavior are reflected in the $\hbar$-dependence of the asymptotic expressions for J_n: they cause the power of $\hbar$ on the right of (6.39) for $\hbar J_n$ to be reduced from $\hbar$ to $\hbar^{2/3}, \hbar^{1/3}$ and $\hbar^0$ for $n = 1, 2$ and 3, respectively. In contrast, because this divergent singularity is absent, the treatment of J_{ns} is similar to that for J_0, and $\hbar J_{ns}$ remains proportional to $\hbar$, making this term asymptotically smaller than the others in the classical limit.

6.5. Summation of all correction terms of $O(\hbar^0)$

We have pointed out that both terms $\mathcal{S}^{(0)}$ and $\hbar\mathcal{S}^{(1)}$ in the first-order corrected expression for $\mathcal{S}(E)$ have portions that are of order $\hbar^0$ and contribute to the classical limit for $\mathcal{S}(E)$. Indeed, each term $\hbar^n\mathcal{S}^{(n)}$ in the expansion (4.24) for $\mathcal{S}(E)$ contains similar contributions that survive as $\hbar \to 0$. Unfortunately, it is very difficult to extend the detailed analysis that we have carried out above to these higher order terms due to the complicated nature of the expressions for $g_t^{(n)}$. Nevertheless, we now show that it is possible to identify the terms in $g_t^{(n)}$ that contribute to the classical limit for $\mathcal{S}(E)$ and to sum all such contributions analytically.

The starting point for our treatment is appendix C which derives expressions for the largest contributions to each correction term $g_t^{(n)}$ near $p = p_c$. These are the portions of $g_t^{(n)}$ that are the most strongly singular (i.e., proportional to $(p - p_c)^{-k}$ with the largest k). The resulting approximation to $\sum_n \hbar^n g_t^{(n)}$ is called $\chi(p)$ (see (C.17)). When this is substituted into (4.24) one obtains

$$\mathcal{S}(E) \approx \mathcal{S}_{\rm sing}(E) \equiv (2\pi i\hbar)^{-1/2} \int_{p_s}^{\infty} dp[\sigma_t(p)]^{1/2}\chi(p)\exp[i\phi(p,p')/\hbar]. \tag{6.41}$$

To evaluate this integral, we deform the integration path to curve C and change the integration variable to v, as in equations (6.20)–(6.26). This gives

$$\mathcal{S}_{\rm sing} = \left[-\frac{3\epsilon}{2\pi i(\epsilon+\delta)}\right]^{1/2} e^{i\phi_c/\hbar} \int_C dv\, v^{1/2} e^{-iv^3} f(v)\chi \tag{6.42}$$

where $f(v)$ was defined in (6.27).

Since we are interested here only in contributions of order $\hbar^0$, we may replace $\epsilon/(\epsilon+\delta)$ in the factor multiplying the integral with unity and neglect all terms proportional to powers of ξ in the expression for $f(v)$. Thus,

$$f(v) = e^{-3i\eta v^2/2} = \sum_{m=0}^{\infty} \frac{(-3i\eta v^2/2)^m}{m!}. \tag{6.43}$$

In the present notation, the expression for χ in (C.17) becomes

$$\chi = \sum_{k=0}^{\infty} d_k i^k v^{-3k}, \tag{6.44}$$

where the coefficients d_k are defined in (C.15).

It is important to remark that, having expressed χ in terms of the variable v, no explicit $\hbar$-dependence appears in (6.44). Consequently, the only $\hbar$-dependence in our result for $\mathcal{S}_{\rm sing}$ will arise from the factor $\exp(i\phi_c/\hbar)$. In contrast, when terms arising from the less strongly singular contributions to $\sum \hbar^n g_t^{(n)}$, that are neglected in χ, are expressed in terms of the integration variable v (see (6.25)), they are found to be proportional to higher powers of $\hbar$. Thus, of all terms in the full correction expression, only those included in χ can contribute to the classical limit for $\mathcal{S}(E)$.

With equations (6.43) and (6.44), (6.42) becomes

$$\mathcal{S}_{\rm sing}(E) \sim e^{i\phi_c/\hbar} \sum_{m=0}^{\infty} \frac{(-3i\eta/2)^m}{m!} G_m \tag{6.45}$$

asymptotically for $\hbar \to 0$, where

$$G_m \equiv \left(-\frac{3}{2\pi i}\right)^{1/2} \sum_{k=0}^{\infty} d_k i^k I_{3k-2m}, \tag{6.46}$$

in terms of the integrals I_m defined in (6.33). Substituting the formulae for these integrals [(6.35)] and for d_k [(C.15)], we obtain

$$G_m = \left(\frac{2}{3\pi}\right)^{1/2} e^{i\pi m/3} \cos(2\pi m/3) \sum_{k=0}^{\infty} \frac{(-1)^k \Gamma(3k+1/2)\Gamma(2m/3-k+1/2)}{54^k k!\Gamma(k+1/2)}, \tag{6.47}$$

which can be recast as

$$\begin{aligned} G_m &= \left(\frac{2}{3\pi}\right)^{1/2} \left(\frac{1}{2}\right) e^{i\pi m/3} \sum_{k=0}^{\infty} \frac{\Gamma(1/6+k)\Gamma(5/6+k)}{k!\Gamma(1/2-2m/3+k)} \left(\frac{1}{2}\right)^k \\ &= \left(\frac{2}{3\pi}\right)^{1/2} \left(\frac{1}{2}\right) e^{i\pi m/3} \frac{\Gamma(1/6)\Gamma(5/6)}{\Gamma(1/2-2m/3)} F(1/6, 5/6; 1/2-2m/3; 1/2), \end{aligned} \tag{6.48}$$

using the triplication formula for gamma functions and the definition of the Gauss hypergeometric function F [34]. For the particular arguments appearing here, the hypergeometric function can be expressed in the closed form as [34]

$$F(1/6,5/6;1/2-2m/3;1/2)=\left(\frac{24}{\pi}\right)^{1/2}\frac{2^{2m/3}\Gamma(1/2-2m/3)\Gamma(m)}{3^{m}\Gamma(m/3)}\times\sin[\pi(1-m)/3]\sin[\pi(2-m)/3], \tag{6.49}$$

where we have used the reflection formula for gamma functions [34]. The sine functions cause this expression to vanish and, therefore, G_m to be zero unless $m = 3\nu$, where $\nu = 0, 1, 2, \ldots$. For the nonvanishing cases we can write

$$F(1/6,5/6;1/2-2\nu;1/2)=\left(\frac{24}{\pi}\right)^{1/2}\left[\frac{2^{2\nu-2}\Gamma(1/2-4\nu)\Gamma(3\nu)}{3^{3\nu-1}\Gamma(\nu)}\right], \tag{6.50}$$

so that we find

$$G_{3\nu}=3\left(-\frac{4}{27}\right)^{\nu}\frac{\Gamma(3\nu)}{\Gamma(\nu)}. \tag{6.51}$$

When this result is substituted in (6.45), we obtain

$$\mathcal{S}_{\rm sing}(E)\sim \mathrm{e}^{\mathrm{i}\phi_c/\hbar}\sum_{\nu=0}^{\infty}\frac{(-3\mathrm{i}\eta/2)^{3\nu}(-4)^{\nu}3\Gamma(3\nu)}{(3\nu)!27^{\nu}\Gamma(\nu)}. \tag{6.52}$$

Noting that $3\Gamma(3\nu)/[(3\nu)!\Gamma(\nu)] = 1/\nu!$, we recognize this sum as the Taylor series for an exponential, so that

$$\mathcal{S}_{\rm sing}(E)\sim \exp(\mathrm{i}\phi_c/\hbar)\exp(-\mathrm{i}\eta^3/2). \tag{6.53}$$

However, using equations (6.29) and (6.24), we find that

$$-\mathrm{i}\frac{\eta^3}{2}=\mathrm{i}\sigma_c'\left(\frac{\delta^3}{6\hbar}\right) \tag{6.54}$$

to lowest order in $\hbar$. Equation (6.6) allows us to express the quantity on the right-hand side of (6.54) in terms of the difference between ϕ_r and ϕ_c. Therefore, to lowest order in $\hbar$,

$$-\mathrm{i}\frac{\eta^3}{2}=\mathrm{i}\frac{(\phi_r-\phi_c)}{\hbar}. \tag{6.55}$$

Substituting this result in (6.53) establishes the asymptotic relation

$$\mathcal{S}_{\rm sing}(E)\sim \exp(\mathrm{i}\phi_r/\hbar)=\mathcal{S}_{psc}(E) \tag{6.56}$$

for $\hbar \to 0$. Thus, summation over an infinite number of terms in the correction series yields the correct semiclassical limiting result for the tunneling amplitude in the Eckart system.

We emphasize that each term $\hbar^n\mathcal{S}^{(n)}$ in the corrected IVR expression for the tunneling amplitude introduces terms that are of *all* orders in $\hbar^{1/3}$. In the above derivation we have selected those that are proportional to $\hbar^0$ and performed the sum analytically. It is interesting that this sum of integrals converges despite the divergence of the sum $\chi(p)$ appearing in the integrand of $\mathcal{S}$ in (6.41). Appendix C notes that the sum for χ is asymptotic to a closed expression involving an Airy function, reminiscent of correction factors appearing in various semiclassical uniform approximations [33, 35]. It is, therefore, disappointing that this explicit formula cannot be simply substituted for $\chi(p)$ in the calculation of $\mathcal{S}_{\rm sing}$. The difficulty is that the condition that $\chi(p)$ be continuous along the entire curve C_1 is incompatible with the condition $|\arg(3\mathrm{i}v^3/2)^{2/3}| < \pi$, which is needed in order that the Airy expression be asymptotically equivalent to χ. Thus, although the Airy formula is highly intriguing, it appears to be of little value. When an infinite number of terms are retained, the proper interpretation of the correction series is as a sum of integrals, as in (4.24), not an integral over a sum or an integral over a function that is asymptotically equivalent to this sum.

7. Discussion

The numerical results presented here verify that the HK and related IVR treatments are inaccurate for the treatment of tunneling in the Eckart system. This is consistent with our analysis which shows that they do not provide proper semiclassical approximations for the tunneling amplitude since they do not tend to the exact result in the limit as $\hbar \to 0$. However, it is found that the description of tunneling is substantially improved for a certain range of energies by adding semiclassical correction terms. The mathematical analysis identifies this range with the condition $\delta = O(\hbar^{1/3})$. Although these energies do not extend too far below the barrier for small $\hbar$, they correspond to tunneling probabilities that may range from values close to one to those that are very small in the classical limit.

The nature of the correction series in this regime is very different from that at higher energies where the transmission across the barrier is classically allowed or only weakly forbidden. At such higher energies, the zeroth-order IVR expression for the tunneling amplitude $\mathcal{S}^{(0)}(E)$ tends to the correct classical limit $\exp(\mathrm{i}\phi_r/\hbar)$ as $\hbar \to 0$. Each higher order term $\hbar^n \mathcal{S}^{(n)}(E)$ in the series is likewise asymptotically equal to $\hbar^n \exp(\mathrm{i}\phi_r/\hbar)$ multiplied by an $\hbar$-independent quantity. Thus, apart from the common factor $\exp(\mathrm{i}\phi_r/\hbar)$, the terms in this series have the same asymptotic $\hbar$-dependence as those in the series $\sum \hbar^n g_t^{(n)}$ in the corrected IVR integrand. As a result, the term $\hbar^n \mathcal{S}^{(n)}$ in (4.24) is, as expected, $O(\hbar^n)$ smaller than the leading term and provides a relatively minor correction to the zeroth-order IVR treatment for small $\hbar$. There are, thus, no real surprises in this case and the behavior of the correction series is analogous to those in other semiclassical contexts such as in the WKB and VVG theories.

However, for lower energies, where the treatment presented in section 6 applies, the zeroth-order term in the IVR treatment of tunneling does not provide the correct classical limit and the higher order terms play a much more important role in achieving accuracy. The leading $\hbar$ dependence of each integral $\hbar^n \mathcal{S}^{(n)}$ is different from that of the quantity $\hbar^n g_t^{(n)}$ appearing in its integrand, due to the singularities in the function $g_t^{(n)}$ at the caustics. Each such term $\hbar^n \mathcal{S}^{(n)}$ can be expanded in a power series containing all positive powers of $\hbar^{1/3}$. In particular, each such term has a component that remains nonzero as $\hbar \to 0$ and contributes to the classical limit. The infinite series of such components, proportional to $\hbar^0$, can be summed and converges to an expression representing the exact PSC formula for the transmission amplitude to lowest order in $\hbar$.

The manner in which the $\hbar$ series works to correct the zero-order IVR estimate and produce the proper classical limit is unexpected. The derivation of the corrections is based on the semiclassical expansion (2.10) for the function $k_t(p, q)$ which may be interpreted physically as the propagator in the particular coherent state-like 'representation' defined by (2.9) [18]. Formulae for the correction terms are obtained by substituting this expansion in the analog of the Schrödinger equation in this representation and identifying coefficients of like powers of $\hbar$ appearing on both sides of the result. The expression $k_t \sim R_t \exp(\mathrm{i}S_t/\hbar)$ is the proper SC limit for k_t and substitution in (2.9) immediately yields the HK approximation for the propagator K_t in the ordinary position representation. However, for the case of tunneling, this approximation is generally not the correct SC limit for K_t. Once the order-by-order correspondence between the $\hbar$-dependence of terms in k_t and K_t is destroyed, it is not at all obvious that the higher order corrections for k_t remain valid corrections for K_t. Thus, the results obtained here could not have been fully anticipated.

Our analysis has been restricted to energy ranges for which the real integration path from p_s to ∞ in the IVR expression can be deformed to the SD path passing through the caustic, as in figure 6. The opposite case, in which the path can be deformed to the SD path through the *root* (as in figure 5) is, in principle, simpler since one can consider δ to be independent of $\hbar$ and apply a standard lowest order SD treatment about the root. As mentioned above, one then finds that the zero-order IVR expression becomes exact as $\hbar \to 0$, and the nth term in the correction series vanishes as $\hbar^n$, just as for the case of classically allowed passage over the barrier. However, this formal analysis does not have immediate implications for numerical results obtained with nonzero $\hbar$. For example, the calculations reported in figure 2, based on the zeroth-order approximation, show no sudden improvement in accuracy as the energy increases past the value ≈0.40 eV where the root and caustic switch positions. The reason is that, for nonzero $\hbar$, the saddles for the root and caustic overlap for this energy range, causing large errors in the lowest order SD treatment. The usual remedy for such problems is to apply some sort of uniformization procedure. An interesting feature of our results is that the higher order corrections continue to improve the accuracy of the IVR treatment in this energy regime despite the apparently inappropriate relative dispositions of the root and caustic points.

The explanation for this continued effectiveness of the correction treatment is that, provided that δ is taken to scale as $\hbar^{1/3}$, the analysis presented in section 6 remains valid even when the real integration path cannot be deformed to the steepest descent curve through the caustic, as was assumed. In more detail, when the integration path can be deformed to the SD path through the root, it might be expected that the asymptotic analysis of J_n requires expansion of the exponential factor $\exp(\mathrm{i}\phi_t/\hbar)$ about $p = p'$ instead of $p = p_c$. However, this is unnecessary. The integration contour that is deformed to pass through $p = p'$ (as in figure 5) can be further deformed to a path that passes near $p = p_c$, similar to C of figure 7. The treatment of section 6, involving expansions about $p = p_c$, can then be applied and the results obtained there remain unchanged. It does not matter for these purposes that C is no longer an SD contour. We recall from equations (6.7)–(6.8) that $\delta = O(\hbar^{1/3})$ implies that the function $\exp(\mathrm{i}\phi_t/\hbar)$ at $p = p'$ can be expanded about $p = p_c$ in powers of $\hbar^{1/3}$. Thus, the asymptotic evaluation of J_n can be equivalently carried out by expanding this exponential about p_c or p'. As a result, our treatment is valid when $|p' - p_c| = O(\hbar^{1/3})$, regardless of the relative dispositions of p' and p_c.

Although the present work has investigated the correction series only for the Eckart system, we believe the basic conclusions to be valid for other unbound one-dimensional systems having barriers. Indeed, preliminary calculations indicate that they apply for multidimensional systems as well. However, the relationship to, and implications for bound systems which exhibit tunneling, such as the double well, [21] are less clear and require further study.

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Appendix A. Reduction to one-dimensional integrals

To show the equivalence, for the present puposes, of the HK propagator to the simpler IVR expression of (4.10), we consider (2.2) with the lower limit for integration over p taken as p_s, as justified in section 4. This allows us to substitute equations (4.6)–(4.9) in (2.6), yielding

$$b_t = \frac{1}{2}\left(1 + \frac{\gamma_1}{\gamma_2} - 2\mathrm{i}\gamma_2 \frac{\partial q_t}{\partial p}\right) \tag{A.1}$$

or

$$b_t = \frac{\gamma_2}{2\gamma}\left(1 - 2\mathrm{i}\gamma \frac{\partial q_t}{\partial p}\right), \tag{A.2}$$

where we have defined

$$\gamma \equiv \frac{\gamma_1\gamma_2}{\gamma_1+\gamma_2}. \tag{A.3}$$

Thus, (2.4) for the HK prefactor becomes

$$R_t = \left(\frac{\gamma_1\gamma_2}{\pi\hbar\gamma}\right)^{1/2}\left(1-2\mathrm{i}\gamma\frac{\partial q_t}{\partial p}\right)^{1/2}. \tag{A.4}$$

Since (4.6) shows that $\partial q_t/\partial p$ is independent of q, R_t is likewise independent of q. In addition, equations (4.5) and (4.3) show that S_t is independent of q and that q_t can be expressed in the form $q_t = q + q_t^{(1)}$, where $q_t^{(1)}$ is independent of q. This allows one to perform the integral over q in (2.2) analytically to obtain

$$\int_{-\infty}^{\infty} \mathrm{d}q\, \mathrm{e}^{-\gamma_2(x'-q-q_t^{(1)})^2/\hbar}\, \mathrm{e}^{\mathrm{i}p(x'-q-q_t^{(1)})/\hbar}\, \mathrm{e}^{-\gamma_1(x-q)^2/\hbar}\, \mathrm{e}^{-\mathrm{i}p(x'-q)/\hbar}$$

$$= \left(\frac{\pi\hbar\gamma}{\gamma_1\gamma_2}\right)^{1/2} \mathrm{e}^{-\gamma(x'-x_t)^2}\, \mathrm{e}^{\mathrm{i}p(x'-x_t)/\hbar} \tag{A.5}$$

where $x_t = x + q_t^{(1)}$ is the position at time t of the particle initiated at x. Due to their independence from q, we can also identify $\partial x_t/\partial p$ as $\partial q_t/\partial p$ and $S_t(p, x)$ as $S_t(p, q)$, which allows us to express

$$K_t(x', x) = \left(\frac{1}{2\pi\hbar}\right)\int_{p_s}^{\infty} \mathrm{d}p \left(1-2\mathrm{i}\gamma\frac{\partial x_t}{\partial p}\right)^{1/2} \mathrm{e}^{-\gamma(x'-x_t)^2}\, \mathrm{e}^{\mathrm{i}p(x'-x_t)/\hbar}\, \mathrm{e}^{\mathrm{i}S_t(p,x)/\hbar}. \tag{A.6}$$

Equation (4.10) is equivalent to this result if the lower limit for integration over p is set to p_s and the conditions described by (4.2) are obeyed. A similar reduction of the HK propagator to a one-dimensional integral was demonstrated by Tanaka [16] for the Hamiltonian $H = -gp^3/3$.

To derive the simplified formula of (4.14) for the scattering amplitude, we substitute (A.6) in (4.15) and perform the Fourier transform to obtain

$$K_t(p', x) = (2\pi\hbar)^{-1}\int_{p_s}^{\infty} \mathrm{d}p[\sigma_t(p)]^{1/2}\, \mathrm{e}^{-(p'-p)^2/(4\gamma\hbar)}\, \mathrm{e}^{-\mathrm{i}p'x_t/\hbar}\, \mathrm{e}^{\mathrm{i}S_t(p,x)/\hbar} \tag{A.7}$$

where

$$\sigma_t(p) = \frac{\partial x_t}{\partial p} + \frac{\mathrm{i}}{2\gamma}. \tag{A.8}$$

Recognizing that

$$\langle p'|\Psi_t\rangle = \int \mathrm{d}x\, K_t(p', x)\langle x|\Psi_0\rangle, \tag{A.9}$$

applying (A.7), and taking into account that the only dependence on x in this propagator expression is through $x_t = x + q_t^{(1)}$, we obtain

$$\langle p'|\Psi_t\rangle = (2\pi\hbar)^{-1}\int_{p_s}^{\infty} \mathrm{d}p[\sigma_t(p)]^{1/2}\, \mathrm{e}^{-(p'-p)^2/(4\gamma\hbar)}\, \mathrm{e}^{-\mathrm{i}p'q_t^{(1)}/\hbar}\, \mathrm{e}^{\mathrm{i}S_t(p,x_0)/\hbar}$$

$$\times \int \mathrm{d}x\, \mathrm{e}^{-\mathrm{i}p'x/\hbar}\langle x|\Psi_0\rangle, \tag{A.10}$$

where x_0 is an arbitrary position obeying the conditions of (4.2). Comparison with (A.7) allows this to be expressed as

$$\langle p'|\Psi_t\rangle = (-2\pi\mathrm{i}\hbar)^{1/2}\, \mathrm{e}^{\mathrm{i}p'x_0/\hbar} K_t(p', x_0)\langle p'|\Psi_0\rangle, \tag{A.11}$$

and substitution of this result in (3.2) yields

$$\mathcal{S}(E) = \lim_{\substack{t\to\infty \\ x_0\to-\infty}} (-2\pi\mathrm{i}\hbar)^{1/2}\, \mathrm{e}^{\mathrm{i}(p'^2t/2m+p'x_0)/\hbar} K_t(p', x_0). \tag{A.12}$$

Appendix B. Formula for $g_t^{(1)}$

Equation (2.15) presents the first-order correction term $g_t^{(1)}$ as the solution of a differential equation. Here we outline the steps needed to express $g_t^{(1)}$ in a useful form as an explicit function plus a remaining integral.

Differentiating Hamilton's equations for q_t and p_t with respect to z yields the following equations for the time derivatives of the quantities c_t and b_t defined in equations (2.16) and (2.6)

$$\dot{c}_t = (b_t + 2\mathrm{i}\gamma_2 c_t)/m, \tag{B.1}$$

$$\dot{b}_t = -2\mathrm{i}\gamma_2 b_t/m + \left(4\gamma_2^2/m - V_2\right)c_t. \tag{B.2}$$

Similarly, differentiating equations (B.1) and (B.2) repeatedly with respect to z gives the equations

$$\begin{aligned} \dot{c}_t' &= (b_t' + 2\mathrm{i}\gamma_2 c_t')/m, \\ \dot{b}_t' &= -2\mathrm{i}\gamma_2 b_t'/m + \left(4\gamma_2^2/m - V_2\right)c_t' - V_3 c_t^2, \\ \dot{c}_t'' &= (b_t'' + 2\mathrm{i}\gamma_2 c_t'')/m, \\ \dot{b}_t'' &= -2\mathrm{i}\gamma_2 b_t''/m + \left(4\gamma_2^2/m - V_2\right)c_t'' - 3V_3 c_t c_t' - V_4 c_t^3. \end{aligned} \tag{B.3}$$

We can now invert these equations to express b_t, c_t and their derivatives with respect to z in terms of the time derivatives. When the resulting formulae are substituted in the right-hand side of (2.15) one obtains, after some manipulation,

$$\frac{\mathrm{d}g_t^{(1)}}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left[\frac{5\mathrm{i}\left(b_t'^2 c_t^2 + b_t b_t' c_t c_t' + b_t^2 c_t'^2\right)}{24(b_t c_t)^3} - \frac{3\mathrm{i}(b_t'' c_t + b_t c_t'')}{24(b_t c_t)^2}\right] + \mathrm{i}\frac{5c_t'^2 - 2c_t c_t''}{8mc_t^4}. \tag{B.4}$$

Both sides of this equation can now be integrated with respect to t. Applying the initial condition $g_0^{(1)} = 0$ then gives the desired result

$$g_t^{(1)} = \frac{5\mathrm{i}\left(b_t'^2 c_t^2 + b_t b_t' c_t c_t' + b_t^2 c_t'^2\right)}{24(b_t c_t)^3} - \frac{3\mathrm{i}(b_t'' c_t + b_t c_t'')}{24(b_t c_t)^2} + I, \tag{B.5}$$

where the remainder term I is defined as

$$I = \mathrm{i}\int_0^t \frac{5c_\tau'^2 - 2c_\tau c_\tau''}{8mc_\tau^4}\,\mathrm{d}\tau. \tag{B.6}$$

Appendix C. The dominant contributions to the correction terms near a caustic

Here we show how the largest contributions to the correction terms $g_t^{(n)}(p)$ in the neighborhood of a caustic p_c can be determined for arbitrary n. Since $g_t^{(n)}(p)$ have pole singularities at $p = p_c$ (see, e.g., (6.15)), we focus attention on the strongest such singularities, i.e., the poles of the highest order, since these dominate the behavior of $g_t^{(n)}(p)$ in this regime.

Consider, first, the first-order correction $g_t^{(1)}$, which is obtained by solving the differential equation (2.11), where the operator $\tilde{L}_t^{(1)}$ is defined in (5.5) of [18]. Since b_t is proportional to $p - p_c$ near the caustic (see (6.13)), the most strongly singular contributions to $g_t^{(1)}$ arise from the particular term in $\tilde{L}_t^{(1)}$ having the form [18]

$$\tilde{L}_t^{(1)} \approx \tilde{D}_t^2\left(\frac{2\gamma^2}{m} - \frac{1}{2}V_2\right), \tag{C.1}$$

where

$$\tilde{D}_t = -\mathrm{i}\frac{\partial}{\partial p}\frac{1}{b_t}. \tag{C.2}$$

To produce the strongest singularity, the operator $\tilde{D}_t^2$ must act directly on the function $b_t^{1/2}$ in (2.11) so that

$$\tilde{L}_t^{(1)} \approx \left(\frac{2\gamma^2}{m} - \frac{1}{2}V_2\right)\tilde{D}_t^2. \tag{C.3}$$

Applying (B.2) we can express the first factor in this equation as

$$\frac{2\gamma^2}{m} - \frac{1}{2}V_2 = \frac{\dot{b}_t}{2c_t} + \frac{\mathrm{i}\gamma b_t}{mc_t} \approx \frac{\dot{b}_t}{2c_t} \tag{C.4}$$

where the approximation follows from the vanishing of b_t at $p = p_c$. Using (4.27) we can further write this result as

$$\frac{2\gamma^2}{m} - \frac{1}{2}V_2 \approx \frac{\dot{b}_t}{2}\left(2\mathrm{i}\gamma + \frac{b_t}{c_t}\right) \approx \mathrm{i}\gamma\dot{b}_t, \tag{C.5}$$

where we have again neglected the term proportional to b_t on the assumption that p is near p_c. Substituting (C.5) in (C.3), defining

$$u = p - p_c, \tag{C.6}$$

and expressing

$$b \approx b_c' u, \qquad \dot{b} = b_c'\dot{u} \tag{C.7}$$

(arising from the Taylor series expansion of b for small u), we obtain

$$\tilde{L}_t^{(1)} \approx -\frac{\mathrm{i}\gamma\dot{u}}{b_c'}\frac{\partial}{\partial u}\frac{1}{u}\frac{\partial}{\partial u}\frac{1}{u}. \tag{C.8}$$

With these approximations, (2.11) becomes

$$\dot{g}_t^{(1)} \approx \dot{g}_t^{(1)}\big|_{\mathrm{sing}} = \left(\frac{5\gamma}{4b_c'}\right)\frac{\dot{u}}{u^4} \tag{C.9}$$

which can be integrated, subject to the initial condition $\dot{g}_0^{(1)} = 0$, to obtain

$$g_t^{(1)}\big|_{\mathrm{sing}} = \left(\frac{5\gamma}{4b_c'}\right)\int_0^t \mathrm{d}t'\frac{\dot{u}}{u^4} = -\frac{5\gamma}{12b_c'u^3}. \tag{C.10}$$

We can now use (6.14) to approximate

$$b_c' \approx \frac{2\mathrm{i}\gamma a}{\epsilon^2}, \tag{C.11}$$

so that our result becomes

$$g_t^{(1)}\big|_{\mathrm{sing}} = \frac{5\mathrm{i}}{24a}\frac{\epsilon^2}{u^3}, \tag{C.12}$$

which is identical to the first term in (6.15).

Analogous expressions for the higher order corrections are obtained by solving (2.12) for $g_t^{(n)}$. Examination of $\tilde{L}_t^{(j)}$ shows that the most strongly singular contributions to this equation come from the term in which $\tilde{L}_t^{(1)}$ acts upon $b_t^{1/2}g_t^{(n-1)}$, so that (2.12) can be approximated as

$$\dot{g}_t^{(n)} \approx \dot{g}_t^{(n)}\big|_{\mathrm{sing}} = \frac{\mathrm{i}}{b^{1/2}}\tilde{L}_t^{(1)}b^{1/2}g_t^{(n-1)}\big|_{\mathrm{sing}}. \tag{C.13}$$

We can now solve this equation for $g_t^{(2)}|_{\text{sing}}$ using equations (C.8) and (C.12) and repeat this procedure recursively to obtain $g_t^{(n)}|_{\text{sing}}$ for arbitrary n. The result, which can be verified by induction, is

$$g_t^{(n)}\big|_{\text{sing}} = d_n \left(\frac{3\mathrm{i}\epsilon^2}{au^3}\right)^n, \tag{C.14}$$

where

$$d_n = \frac{\Gamma(3n+1/2)}{54^n n!\Gamma(n+1/2)}. \tag{C.15}$$

The sum of the most singular contributions to the correction terms

$$\chi(p) \equiv \sum_{n\geqslant 0} \hbar^n g_t^{(n)}\big|_{\text{sing}} \tag{C.16}$$

thus has the form

$$\chi(p) = \sum_{n\geqslant 0} d_n(-\zeta)^{-n}, \tag{C.17}$$

where

$$\zeta = \frac{\mathrm{i}a(p-p_c)^3}{3\hbar\epsilon^2}. \tag{C.18}$$

It is interesting to observe that this divergent sum is an asymptotic series for the Airy function [34]

$$2\pi^{1/2}(3\zeta/2)^{1/6}e^{\zeta}\,\mathrm{Ai}[(3\zeta/2)^{2/3}] \sim \chi(p), \tag{C.19}$$

which is valid as $\hbar \to 0$ for $|\arg(3\zeta/2)^{2/3}| < \pi$. Thus, the expression appearing on the left-hand side of (C.19) can be regarded as a summed form of χ. The possible usefulness of this result is discussed in the text.

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