Thermal rate of transmission through a barrier: Exact expansion of up to and including terms of order $\hbar^4$

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Nine decades after Wigner's formulation of quantum rate theory, his celebrated result was recently generalized to the asymmetric barrier using an exact first-order expansion of the transmission probability in terms of $\hbar^2$. This paper extends the first-order quantum correction to second-order correction of order $\hbar^4$ for the thermally averaged transmission probability through an arbitrary barrier. The derivation employs a systematic expansion of the projection operator onto products and the thermal distribution which involves a Taylor expansion of the potential about the barrier up to eighth order. The resulting exact analytical expression is calibrated with numerical calculations of several model potentials and shows excellent agreement when the $\hbar^4$ term is included. In comparison, the semiclassical transition state theory cannot reproduce the correct $\hbar^4$ terms when the anharmonicity is treated on the level of VPT-4 (vibrational perturbation theory—fourth order) and will potentially need a VPT-6 expansion. Further analysis of the quartic barrier reveals suppressed transmission due to the dominant role of quantum reflection above the barrier. These results not only provide a conceptual framework but can also be applied to heavy atom tunneling and machine learning.

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I. INTRODUCTION

Wigner wrote two seminal papers in 1932 [1,2]. In one of them [1] he defined what is known today as the Wigner representation in phase space and used it do derive a perturbation theory expression for the thermal density $\exp(-\beta\hat{H})$ [with $\beta = 1/(k_B T)$ the inverse temperature and $\hat{H}$ the Hamiltonian operator]. In the second [2], Wigner used his phase-space approach to derive a leading-order correction, of the order of $\hbar^2$, to the thermal rate of transmission of a particle of mass M through a barrier potential $V(q)$. He derived the exact leading-order expression for a smooth symmetric barrier, but, not less important, used what is known today as classical Wigner dynamics [3,4], to derive a more approximate expression, which to order $\hbar^2$ is identical to the transmission probability for a parabolic barrier. Very recently, we generalized Wigner's result to include asymmetric barriers [5], the result for the transmission factor (ratio of quantum to classical thermal flux through the barrier) being

$$\kappa_2 = \frac{\hbar^2\beta^2\omega^2}{24}\left[1 + \frac{1}{4}\left(\frac{V_4}{\beta V_2^2} - \frac{V_3^2}{3\beta V_2^3}\right)\right] \tag{1.1}$$

where the potential, whose single barrier is located at $q = 0$, is expanded as

$$V(q) = \sum_{j=2}^{\infty} V_j \frac{q^j}{j!} \tag{1.2}$$

and the second derivative defines a barrier frequency

$$V_2 = -M\omega^2. \tag{1.3}$$

Wigner, in his paper [2], considered that the nonlinear correction to the parabolic barrier estimate will be small and so is really not too important. Furthermore, he was concerned that his expression would diverge if the barrier frequency ω went to zero. We note a few other points. Typically, one expects that nonlinearity broadens the potential barrier and this broadening would cause tunneling to be more difficult and hence the transmission factor would be reduced, relative to the parabolic barrier result. However, as seen from the exact result to order $\hbar^2$ [Eq. (1.1)], if, in the symmetric case, $V_4 \geqslant 0$ the leading-order correction increases the transmission factor. Not less important is the fact that many of the well-known approximations to the thermal rate, such as classical Wigner dynamics [3,4], centroid molecular dynamics [6], and ring polymer molecular dynamics [7], do not reduce to this correct limit. Third, and this Wigner could not have known in his time, the transmission probability for many heavy atom tunneling systems [8–10] is dominated by the leading-order term of order $\hbar^2$ and furthermore the transmission coefficients are typically in the range of 1–5. In this range, ignoring the nonlinear contributions can cause a serious error in the estimation of the rate.

There is another aspect of recent interest in the expansion in terms of $\hbar^{2n}$. To date, except for the parabolic barrier, no attempt has been made, even in one dimension, to derive an exact analytic expression for the transmission factor, valid for all orders of $\hbar^{2n}$ and all temperatures. The parabolic barrier result becomes inapplicable in the deep tunneling regime since it diverges at the well-known and understood crossover temperature ($\hbar\beta_c\omega = 2\pi$) [11–13]. The analytic expression for the energy dependent transmission coefficient for an Eckart barrier is known [14], but its thermal average is not, even in the symmetric case. Especially in view of machine learning algorithms for reaction rates [15], such an expression would be valuable, as it could be used to "teach" the algorithm the correct answer for a broad range of physically significant properties such as the barrier height, exoergicity, and other parameters of the potential. In this context, an approximate analytic expression for the thermal rate, valid (but not exact) for all temperatures, has been derived recently [16]. The exact expression for the expansion of the rate in terms of $\hbar^{2n}$ for $n = 1, 2, \ldots$ can be incorporated within the analytic theory, to give a result which is rather accurate over a wide range of conditions and which may then be used within a machine learning context.

An important development of the past decade or so has been the development of a semiclassical thermal rate theory for the transmission coefficient [17–20]. In contrast to all other approximations in use, it is exact up to order $\hbar^2$, but it remains an open question whether the semiclassical approach can be accurately extended to higher order.

The goal of the present paper is to answer some of these challenges. In Sec. II we derive the exact correction term of order $\hbar^4$; we do this for a "normal" barrier potential in which the second-order derivative at the barrier is finite. We find that the semiclassical theory of Ref. [19] is not sufficient to this order and that, in principle, this fourth-order-in-$\hbar$ term needs as input the first eight derivatives of the potential at the barrier and not only the first six derivatives as in the theory of Ref. [19]. We then study a purely quartic barrier, where we find that its $\hbar^2$ term vanishes, but the term of order $\hbar^4$ is negative, indicating that there are cases where quantum mechanics through quantum reflection may reduce the transmission coefficient, as compared to its classical limit. Finally, out of curiosity, we also study the case of a purely hexic barrier and find that for such a broad barrier the leading correction term is at least of order $\hbar^6$.

In Sec. III we apply these results to two classes of potential barriers. One is the Eckart barrier, where as already mentioned the energy dependent transmission coefficient is known analytically [14], so that the thermal transmission coefficient may be obtained numerically accurately to provide a numerical test of the validity of our analytic expression. We then use the known exact coefficients of order $\hbar^2$ and $\hbar^4$ within the context of the analytic semiclassical rate theory of Ref. [16] to show that they allow extension of the analytic rate theory to rather low temperatures, both for the symmetric and asymmetric Eckart barriers. The second potential to be studied is what we will refer to as a "tanh barrier" where the second derivative is always negative but the fourth derivative may change sign when the distance parameter of the potential is increased, making its form similar to a square barrier potential. In this case, the negativity of the fourth derivative leads to a negative contribution to the transmission coefficient, indicating that, as for a purely quartic potential, quantum reflection above the barrier can be a dominant contribution. This observation should be of special interest when considering for example tunneling through quantum dots. We end with a discussion, paying attention to the possibility of extension of the present derivation also to multidimensional systems.

II. DERIVATION OF THE $\hbar^4$ CONTRIBUTION TO THE THERMAL TRANSMISSION COEFFICIENT

A. Preliminaries

We assume a one-dimensional Hamiltonian operator

$$\hat{H} = \frac{\hat{p}^2}{2M} + V(\hat{q}) \tag{2.1}$$

where the potential has a barrier at the coordinate location $q = 0$ with energy $V(0) = 0$, and $(\hat{p}, \hat{q})$ denotes the momentum and coordinate operators, respectively. The flux operator is defined as

$$\hat{F}(\hat{q}) = \frac{1}{2M}[\hat{p}\delta(\hat{q}) + \delta(\hat{q})\hat{p}] \tag{2.2}$$

where $\delta(x)$ denotes the Dirac "delta" function. The transmission coefficient is defined as the ratio of the exact quantum thermal flux through the barrier to the classical thermal flux:

$$\kappa = 2\pi\hbar\beta \mathrm{Re}(\mathrm{Tr}[\exp(-\beta\hat{H})\hat{F}(\hat{q})\hat{P}]) \tag{2.3}$$

where the projection operator onto the product side is defined as

$$\hat{P} = \lim_{t\to\infty}\left[\exp\left(\frac{i\hat{H}t}{\hbar}\right)\theta(\hat{q})\exp\left(-\frac{i\hat{H}t}{\hbar}\right)\right] \tag{2.4}$$

and $\theta(\hat{q})$ is the unit step function.

The Wigner representation in one-dimensional phase space of an operator $\hat{O}$ is defined as

$$O(p,q) = \int_{-\infty}^{\infty} d\xi \exp\left(\frac{ip\xi}{\hbar}\right)\left\langle q - \frac{\xi}{2}\right|\hat{O}\left|q + \frac{\xi}{2}\right\rangle. \tag{2.5}$$

Two properties of Wigner functions of operators will be used to derive the $\hbar^4$ term: (i) the trace operation of two operators is just the phase-space integration of the separate Wigner representation of the two operators

$$\mathrm{Tr}[\hat{A}\hat{B}] = \int_{-\infty}^{\infty}\frac{dpdq}{2\pi\hbar}A(p,q)B(p,q) \tag{2.6}$$

and (ii) the Wigner representation of a product of operators

$$\hat{C} = \hat{A}\hat{B} \tag{2.7}$$

in terms of the representation of the separate operators is given by [21]

$$C(p,q) = A(p,q)\exp\left[\frac{i\hbar}{2}\hat{\Lambda}\right]B(p,q) \tag{2.8}$$

where the Janus operator $\hat{\Lambda}$ is defined as

$$\hat{\Lambda} = \left(\frac{\overleftarrow{\partial}}{\partial q}\frac{\overrightarrow{\partial}}{\partial p} - \frac{\overleftarrow{\partial}}{\partial p}\frac{\overrightarrow{\partial}}{\partial q}\right) \tag{2.9}$$

and the right and left arrows denote derivative of the functions to the right and left of the operator, respectively. We will need to employ Eq. (2.8) since the expression for the transmission coefficient [Eq. (2.3)] involves a product of three operators.

The exact Wigner representation of the flux operator is

$$F(p,q) = \frac{p}{M}\delta(q). \tag{2.10}$$

We will also assume the following formal expansion:

$$\Omega(p,q) \equiv \exp(-\beta\hat{H})(p,q) = \sum_{n=0}^{\infty} \hbar^{2n}\Omega_n(p,q). \tag{2.11}$$

Wigner, in his 1932 paper [1], provided explicit expressions for the first three terms:

$$\Omega_0(p,q) = \exp\left[-\beta\left(\frac{p^2}{2M} + V(q)\right)\right], \tag{2.12}$$

$$\Omega_1(p,q) = \Omega_0(p,q)\left(\frac{1}{8}V''(q)\left[-\frac{\beta^2}{M} + \left(\frac{\beta^3 p^2}{3M^2}\right)\right] + \frac{\beta^3 V'^2(q)}{24M}\right), \tag{2.13}$$

and

$$\begin{aligned}\Omega_2(p,q) = {}& \frac{\beta^2\Omega_0(p,q)}{16M^2}\left\{4\frac{\beta^2p^4}{4M^2} - 12\frac{\beta p^2}{2M} + 3\right\}\left(\frac{\beta^2 V''^2(q)}{72} - \frac{\beta V^{(4)}(q)}{120}\right)\\ &+ \frac{\beta^2\Omega_0(p,q)}{64M^2}\left\{4\frac{\beta p^2}{2M} - 2\right\}\left(\frac{\beta^3 V''(q)V'^2(q)}{18} - 2\frac{\beta^2 V''^2(q)}{15} - \frac{\beta^2 V'(q)V^{(3)}(q)}{15} + \frac{\beta V^{(4)}(q)}{15}\right)\\ &+ \frac{\beta^3\Omega_0(p,q)}{64M^2}\left(\frac{\beta^3 V'^4(q)}{18} - \frac{22\beta^2 V''(q)V'^2(q)}{45} + \frac{2\beta V''^2(q)}{5} + \frac{8\beta V'(q)V^{(3)}(q)}{15} - \frac{4V^{(4)}(q)}{15}\right).\end{aligned} \tag{2.14}$$

Similarly, the projection operator may be expanded as

$$P(p,q) = \sum_{n=0}^{\infty} \hbar^{2n}P_n(p,q) \tag{2.15}$$

and we know that the zeroth-order classical projection operator is

$$P_0(p,q) = \theta(-q)\theta(p - \sqrt{-2MV(q)}) + \theta(q)\theta(p + \sqrt{-2MV(q)}). \tag{2.16}$$

Henceforth to keep the notation as simple as possible we will always assume that $q \geqslant 0$ so that only the second term will be of importance. We also know from Ref. [22] that

$$P_1(p,q) = g_{21}(q)\delta''(p + \sqrt{-2MV(q)}) + g_{11}(q)\delta'(p + \sqrt{-2MV(q)}) + g_{01}(q)\delta(p + \sqrt{-2MV(q)}) \tag{2.17}$$

where the functions g_{j1}, $j = 0, 1, 2$ are

$$g_{21}(q) = \frac{M}{24\sqrt{-2MV(q)}}\left(V''(q) - \frac{[V'(q)]^2}{2V(q)}\right), \tag{2.18}$$

$$g_{11}(q) = \frac{1}{24V(q)}\left(V''(q) - \frac{3[V'(q)]^2}{4V(q)} - \frac{1}{2}M\omega^2\right), \tag{2.19}$$

$$g_{01}(q) = -\frac{1}{\sqrt{-2MV(q)}}(g_{11}(q) - g_{11}(0)). \tag{2.20}$$

For future use we note that

$$g_{21}(0) \equiv \lim_{q\to 0} g_{21}(q) = \frac{V_3}{72\omega}, \tag{2.21}$$

$$g_{11}(0) \equiv \lim_{q\to 0} g_{11}(q) = -\frac{1}{96V_2}\left(V_4 - \frac{V_3^2}{3V_2}\right), \tag{2.22}$$

$$g_{01}(0) \equiv \lim_{q\to 0} g_{01}(q) = \frac{2V_3}{3V_2^2}\omega g_{11}(0), \tag{2.23}$$

and

$$g''_{11}(0) = \frac{-3V_2^3V_6 + 5V_2^2V_3V_5 - 3V_2^2V_4^2 - 7V_2V_3^2V_4 - 2V_3^4}{864V_2^4} = -2M\omega g'_{01}(0). \tag{2.24}$$

To obtain the expression for the transmission factor up to order $\hbar^4$ we rewrite the exact expression

$$\kappa = \beta\int_{-\infty}^{\infty} dpdq\left[\frac{p}{M}\delta(q)\exp\left[\frac{i\hbar}{2}\hat{\Lambda}\right]\Omega(p,q;\beta)\right]P(p,q) = 1 + \kappa_2 + \kappa_4 + O(\hbar^6). \tag{2.25}$$

The term of order $\hbar^2$ has in principle three contributions

$$\kappa_2 = \hbar^2\beta \int_{-\infty}^{\infty} dpdq \frac{p}{M}\delta(q)[\Omega_0(p,q;\beta)P_1(p,q) + \Omega_1(p,q;\beta)P_0(p,q)] - \frac{\hbar^2\beta}{4}\int_{-\infty}^{\infty} dpdq\Big[\frac{p}{4M}\delta(q)\hat{\Lambda}^2\Omega_0(p,q;\beta)\Big]P_0(p,q) \tag{2.26}$$

and the result is given in Eq. (1.1). The $\hbar^4$ contribution to the transmission coefficient consists of six terms:

$$\begin{aligned}\kappa_4 =& \frac{\hbar^4\beta}{16\times 24}\int_{-\infty}^{\infty} dpdq\Big[\frac{p}{M}\delta(q)\hat{\Lambda}^4\Omega_0(p,q;\beta)\Big]P_0(p,q) + \hbar^4\beta\int_{-\infty}^{\infty} dpdq\frac{p}{M}\delta(q)\Omega_0(p,q;\beta)P_2(p,q)\\ &+ \beta\hbar^4\int_{-\infty}^{\infty} dpdq\Big[\frac{p}{M}\delta(q)\Omega_2(p,q;\beta)\Big]P_0(p,q) - \frac{\hbar^4\beta}{8}\int_{-\infty}^{\infty} dpdq\Big[\frac{p}{M}\delta(q)\hat{\Lambda}^2\Omega_0(p,q;\beta)\Big]P_1(p,q)\\ &- \frac{\beta\hbar^4}{8}\int_{-\infty}^{\infty} dpdq\Big[\frac{p}{M}\delta(q)\hat{\Lambda}^2\Omega_1(p,q;\beta)\Big]P_0(p,q) + \beta\hbar^4\int_{-\infty}^{\infty} dpdq\frac{p}{M}\delta(q)\Omega_1(p,q;\beta)P_1(p,q)\\ &\equiv \kappa_{41}+\kappa_{42}+\kappa_{43}+\kappa_{44}+\kappa_{45}+\kappa_{46}.\end{aligned} \tag{2.27}$$

B. The $\hbar^4$ contribution to the transmission factor

1. κ_{41}

We will consider the contributions term by term, as defined in Eq. (2.27). Since the flux operator is linear in the momentum, it is a matter of some straightforward algebra to see that

$$\Big[\frac{p}{M}\delta(q)\hat{\Lambda}^4\Omega_0(p,q;\beta)\Big] = -\frac{4}{M}\frac{\partial^4\Omega_0(p,q)}{\partial p^3\partial q}\delta^{(3)}(q) + \frac{\partial^4\Omega_0(p,q)}{\partial p^4}\frac{p}{M}\delta^{(4)}(q). \tag{2.28}$$

It is then a matter of carrying out systematic integrations by parts, to remove the derivatives of the spatial delta function. One finds

$$\kappa_{41} = 0. \tag{2.29}$$

2. κ_{42}

Here, the missing ingredient is the $\hbar^4$ contribution to the projection operator $P_2(p,q)$. This is arguably the most involved part of the derivation. Here we bring the main results, and details are given in Appendix A. One finds that the $\hbar^4$ contribution may be written as

$$P_2(p,q) = \sum_{j=0}^{5} g_{j2}(q)\delta^{(j)}(p_{sx}) \tag{2.30}$$

where the jth-order derivative denoted as a superscript in parentheses is with respect to the argument and

$$p_{sx} = p + \sqrt{-2MV(q)} \tag{2.31}$$

is the analytic expression for the separatrix between reactive and unreactive trajectories in phase space. The solution for $P_2(p,q)$ given in Eq. (2.30) when inserted into the definition of κ_{42} given in Eq. (2.27), assuming that the spatial coefficients do not diverge when $q\to 0$, gives

$$\kappa_{42} = \hbar^4\beta^4\omega^4\Big[-\frac{Mg_{12}(0)}{\beta^3V_2^2} + \frac{3g_{32}(0)}{\beta^2V_2^2} - \frac{15g_{52}(0)}{M\beta V_2^2}\Big] \equiv \kappa_{421}+\kappa_{423}+\kappa_{425}. \tag{2.32}$$

As shown in Appendix A,

$$g_{52}(0) = -\frac{MV_3^2}{18\times 24^2V_2}, \tag{2.33}$$

$$g_{32}(0) = \frac{216V_2^3V_6 + 552V_2^2V_3V_5 + 405V_2^2V_4^2 + 870V_2V_3^2V_4 + 245V_3^4}{2\,488\,320V_2^4}, \tag{2.34}$$

$$\begin{aligned}g_{12}(0) =& \frac{135V_2^5V_8 + 420V_2^4V_3V_7 + 810V_2^4V_4V_6 + 597V_2^4V_5^2}{4\,147\,200MV_2^7} + \frac{1020V_2^3V_3^2V_6 + 3570V_2^3V_3V_4V_5 + 675V_2^3V_4^3}{4\,147\,200MV_2^7}\\ &- \frac{-2140V_2^2V_3^3V_5 - 4125V_2^2V_3^2V_4^2 - 3400V_2V_3^4V_4 - 700V_3^6}{4\,147\,200MV_2^7}.\end{aligned} \tag{2.35}$$

For a symmetric barrier the expression simplifies significantly to

$$\kappa_{42,\mathrm{sym}} = -\hbar^4\beta^4\omega^4 \frac{V_2^2 V_8 + 6V_2V_4V_6 + 5V_4^3}{30\,720\beta^3 V_2^6} + \hbar^4\beta^4\omega^4 \frac{15V_4^2 + 8V_2V_6}{30\,720\beta^2 V_2^4}. \tag{2.36}$$

3. κ_{43}

The expression for $\Omega_2(p,q)$ has already been given in Eq. (2.14) so that it is straightforward to find that

$$\kappa_{43} = \frac{7\hbar^4\beta^4\omega^4}{60\times 96} - \frac{\hbar^4\beta^4\omega^4}{640}\frac{V_4}{\beta V_2^2}. \tag{2.37}$$

The first term on the right-hand side is the parabolic barrier contribution, and the second term is a correction due to the anharmonicity. Any asymmetry in the potential does not contribute to this term.

4. κ_{44}

Obtaining the expression for this term is rather lengthy, and the details are given in Appendix B. The result is rather simple:

$$\kappa_{44} = \frac{\hbar^4\beta^4\omega^4}{64}\frac{V_4}{\beta V_2^2}. \tag{2.38}$$

5. κ_{45}

Derivation of the expression for κ_{45} is detailed in Appendix C and one finds

$$\kappa_{45} = -\frac{\beta^4\hbar^4\omega^4}{64}\left(\frac{V_4}{\beta V_2^2}\right). \tag{2.39}$$

6. κ_{46}

The last term involves only the $\hbar^2$ contribution to the thermal distribution and the projection operator, and the integration is straightforward, giving

$$\kappa_{46} = \frac{\hbar^4\beta^4\omega^4}{8\times 96}\left(\frac{V_4}{\beta V_2^2} + \frac{V_3^2}{3\beta V_2^3}\right). \tag{2.40}$$

7. κ_4

Putting it all together we find that

$$\kappa_4 = \kappa_{421} + \kappa_{423} + \frac{7\hbar^4\beta^4\omega^4}{60\times 96} - \frac{\hbar^4\beta^4\omega^4}{3840}\frac{V_4}{\beta V_2^2} - \frac{7\hbar^4\beta^4\omega^4}{6912}\frac{V_3^2}{\beta V_2^3} \tag{2.41}$$

where the expressions for κ_{421} and κ_{423} are given in Eqs. (2.32), (2.34), and (2.35). Equation (2.41) is a central result of this paper. For symmetric barriers it reduces to

$$\kappa_{4,\mathrm{sym}} = \frac{7\hbar^4\beta^4\omega^4}{60\times 96} - \frac{\hbar^4\beta^4\omega^4}{3840}\frac{V_4}{\beta V_2^2} + \frac{\hbar^4\beta^4\omega^4}{6\times 24^2}\left[\frac{405V_4^2 + 216V_2V_6}{240\beta^2 V_2^4}\right] - \hbar^4\beta^4\omega^4 \frac{V_2^2V_8 + 6V_2V_4V_6 + 5V_4^3}{5\times 6144\beta^3 V_2^6}. \tag{2.42}$$

One notes that the $\hbar^4$ correction, in principle, calls for knowledge of up to the eighth derivative of the potential at the barrier top and that moreover the term with V_8 may become dominant at high temperatures, since it is linear in the inverse temperature β. The high-order derivatives are associated with the $\hbar^4$ term of the projection operator, demonstrating the need to treat the projection operator correctly; this is not done in all approximate methods that use the flux side formalism to estimate the rate.

C. Semiclassical rate theory with VPT-4

The semiclassical method of Refs. [17–20] is different, as the semiclassical approximation is based on an energy dependent estimate of the transmission probability

$$T_{\mathrm{SC}}(E) = \frac{1}{1+\exp[2\phi(E)]} \tag{2.43}$$

where ϕ is the classical (imaginary) action across the barrier. Using the VPT-4 (vibrational perturbation theory—fourth order) version of the theory as given in Ref. [19] one finds that the $\hbar^4$ correction is

$$\frac{\kappa_4(\mathrm{SC})}{\hbar^4\beta^4\omega^4} = \frac{7}{96\times 60} - \frac{1}{3840}\frac{V_4}{\beta V_2^2} + \frac{7}{6912}\frac{V_3^2}{\beta V_2^3} - \frac{1}{3840}\frac{V_6}{\beta^2 V_2^3} + \frac{9V_4^2}{288\times 64\beta^2 V_2^4} - \frac{49}{30\times 8\times 288}\frac{V_3V_5}{\beta^2 V_2^4} + \frac{95V_3^2V_4}{288\times 24\times 8\beta^2 V_2^5} - \frac{287V_3^4}{144\times 288\times 8\beta^2 V_2^6} \tag{2.44}$$

and this should be compared with the exact result, as given in Eq. (2.41), which may be rewritten for the sake of comparison as

$$\frac{\kappa_4}{\hbar^4\beta^4\omega^4} = \frac{7}{60\times 96} - \frac{1}{3840}\frac{V_4}{\beta V_2^2} + \frac{7}{6912}\frac{V_3^2}{\beta V_2^3} - \frac{1}{3840}\frac{V_6}{\beta^2 V_2^3} + \frac{1}{64\times 288}\frac{9V_4^2}{\beta^2 V_2^4} + \frac{46}{288\times 8\times 30}\frac{V_3V_5}{\beta^2 V_2^4} - \frac{58}{8\times 288\times 24}\frac{V_3^2V_4}{\beta^2 V_2^5} + \frac{98}{144\times 8\times 288}\frac{V_3^4}{\beta^2 V_2^6} + \frac{\kappa_{421}}{\hbar^4\beta^4\omega^4}. \tag{2.45}$$

One notes that the κ_{421} term is missing in the VPT-4 theory. Second, although the upper two lines in Eq. (2.44) are the same as the upper two lines in the exact result as given in Eq. (2.45), the coefficients of the rest of the terms are incorrect. The semiclassical VPT-4 theory is based on expanding the energy to third order in the action; this is insufficient and is the source of the error. To obtain the correct $\hbar^4$ result for the transmission factor it must be expanded to fourth order in the action and this would be a VPT-6 semiclassical theory. We also note, as described in Appendix D, that the VPT4 results for the transmission coefficient can lead to situations where the action at high energies goes to minus infinity, leading to a vanishing transmission coefficient, and this is of course incorrect. This too would be corrected if the energy is expanded to fourth order in the action, i.e., using what would be appropriately called a VPT-6 theory.

D. The quartic barrier

As mentioned in the Introduction, some of the expressions derived thus far will seemingly diverge if the second-order derivative vanishes. As shown in Appendix E, this case must be dealt with separately and one then obtains expressions which are finite, with all divergences removed. For the quartic barrier, the second-order $\hbar^2$ contribution to the transmission coefficient vanishes, while the fourth-order $\hbar^4$ correction is finite:

$$\kappa_2(\text{quartic barrier}) = 0, \tag{2.46}$$

$$\kappa_4(\text{quartic barrier}) = -\frac{8\hbar^4\beta^3 V_4}{5\times 24^2 M^2}. \tag{2.47}$$

This result is instructive. The quartic barrier is thicker than the parabolic barrier, hence it is more classical in nature. One must go to fourth order in $\hbar$ before finding any quantum correction to the classical transmission factor. Moreover, here for the first time we see that the leading-order term is negative as a result of the dominance of quantum reflection. This also implies an inverse isotope effect as the term is inversely proportional to the mass squared. Increasing the mass will make the system more classical and will reduce the effect of quantum reflection.

E. The hexic barrier

As might be expected, based on the results for the quartic barrier, for a purely hexic barrier the $\hbar^4$ contribution vanishes. However, the derivation is not trivial, since the individual $g_{j1}(q)$ and $g_{j2}(q)$ functions may diverge at the barrier. To eliminate the divergence, one must first sum over all terms and only then integrate over the coordinate. As shown in Appendix F, this then leads to the result that up to and including fourth-order terms in $\hbar$ one finds a vanishing contribution to the transmission factor. This is perhaps not surprising, as the hexic barrier is broader than the quartic barrier so that it can be considered as being more classical.

III. NUMERICAL IMPLEMENTATIONS

A. Eckart barrier

To get a better feeling for the $\hbar^4$ term we consider the asymmetric Eckart barrier whose form is

$$V(q) = \frac{v_1 - v_2}{1+\exp\left(-\frac{q}{d}\right)} + \frac{(\sqrt{v_1}+\sqrt{v_2})^2}{4\cosh^2(\frac{q}{d})} \tag{3.1}$$

where v_1 is the barrier height, v_2 defines the exoergicity of the potential, and d is a length scale. For the symmetric Eckart barrier (with $d = 1$) one finds that

$$V_2 = -\frac{v_1}{2}, V_4 = v_1, V_6 = -\frac{17}{4}v_1, V_8 = 31v_1 \tag{3.2}$$

so that for the symmetric barrier the coefficient κ_4 reduces to the relatively simple expression

$$\kappa_{4,\text{sym}}(\text{Eckart barrier}) = \frac{7\hbar^4\beta^4\omega^4}{60\times 96} - \frac{\hbar^4\beta^4\omega^4}{960}\frac{1}{\beta v_1} - \frac{\hbar^4\beta^4\omega^4}{960\beta^2 v_1^2}. \tag{3.3}$$

Comparing this to the result obtained by Yasumori [23] [Eq. (3.23) of Ref. [16]] which is

$$\kappa_{4,\text{sym}}(\text{Eckart barrier, Yasumori}) = \frac{7\hbar^4\beta^4\omega^4}{60\times 96} - \frac{\hbar^4\beta^4\omega^4}{960}\frac{1}{\beta v_1} + \frac{\hbar^4\beta^4\omega^4}{640}\frac{1}{\beta^2 v_1^2} \tag{3.4}$$

we note that the last term is incorrect. Yasumori used an approximate expression for the energy dependent transmission coefficient which leads to the correct κ_2 but not κ_4. The difference however is not necessarily large as the erroneous term goes as $\frac{1}{\beta^2 v_1^2}$ and under normal circumstances this will give only a small contribution. For the symmetric Eckart barrier, the VPT-4 expression for the rate [Eq. (2.44)] leads to the correct result for κ_4, indicating that the Eckart barrier has special symmetries in its structure, which are not necessarily there in a realistic potential.

Since the energy dependent transmission coefficient is known, one may obtain the numerically exact thermal transmission coefficient with a single quadrature. This then serves as a check on the correctness of our result for κ_4 as well as getting a feeling for the magnitude of the coefficient and under what circumstances the first two terms are sufficient to obtain the overall transmission coefficient.

In Fig. 1, we plot the exact transmission factor (solid line), the second-order transmission factor (dashed line), and the fourth-order result (dotted line) for a reduced barrier height of $\beta v_1 = 3$ and various asymmetries $\frac{v_2}{v_1} = 1, 3, 5$ as one goes from left to right as a function of the reduced value $\alpha = \frac{\hbar}{M\omega d^2}$. One notices that adding the $\hbar^4$ term significantly improves the accuracy as compared to the theory with only the $\hbar^2$ term. The same is shown in Fig. 2 but for a reduced barrier height of $\beta v_1 = 1$. Note that the range of α^2 values is four times larger in Fig. 2 than in Fig. 1.

A different numerical test of the analytic $\hbar^4$ correction term is to consider the following quantity:

$$\Delta\kappa_4 \equiv \kappa - 1 - \kappa_2 \tag{3.5}$$

which for small enough values of $\hbar$ should scale linearly with $\hbar^4$ or equivalently with the reduced $\hbar^4$ parameter α^4. In Figs. 3 and 4 we plot $\Delta\kappa_4$ for the cases studied in Figs. 1 and 2. One notes that in all cases, the initial slope is correctly predicted by the $\hbar^4$ term. Furthermore, the best results are found for the symmetric barrier. It would seem that asymmetry in the barrier magnifies the dependence of the transmission coefficient on higher-order terms in $\hbar$. An even more stringent test of the correctness of the $\hbar^4$ term is to consider $\lim_{\alpha\to 0}\frac{\Delta\kappa}{\alpha^4}$ and compare this with $\frac{\kappa_4}{\alpha^4}$. The results are given in tabular form in Table I and provide numerical evidence for the accuracy of the $\hbar^4$ term.

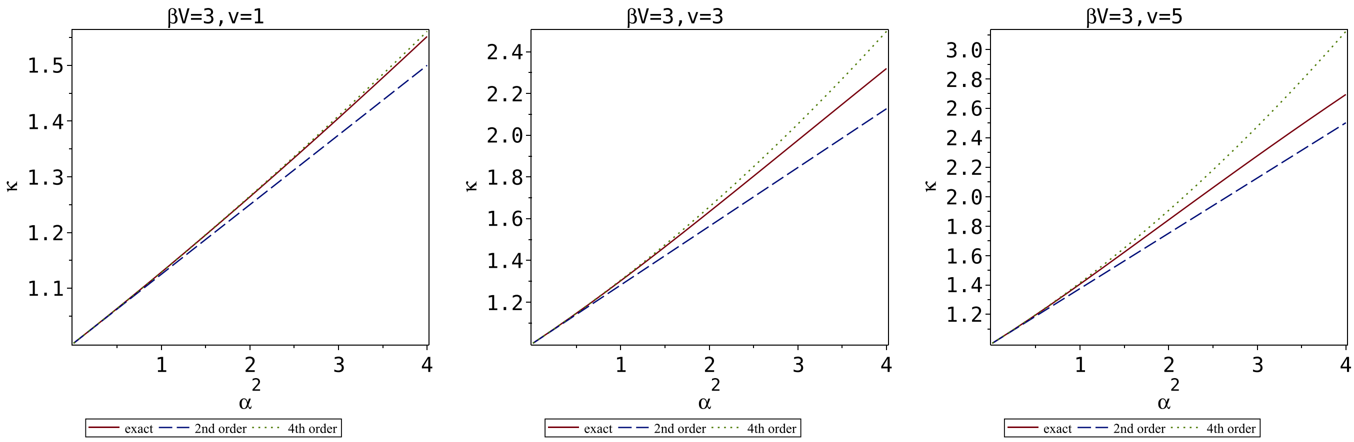

FIG. 1. $\hbar^4$ expansion of the transmission coefficient for the Eckart barrier. In all panels, the solid line is the numerically exact transmission factor, the dotted line is the analytical result including terms up to $\hbar^4$, and the dashed line is the contribution from the analytical result but only including terms up to $\hbar^2$. In all three panels the reduced barrier height is 3 while the asymmetry parameter $v = v_2/v_1$ varies from unity (symmetric potential) to 3 to 5 as one goes from left to right.

B. Application to thawed Gaussian rate theory

As shown in Ref. [16], using the coherent-state representation of the flux side expression for the transmission factor and approximating the thermal distribution and the real time propagator with thawed Gaussians, one finds that the transmission coefficient for such a theory is

$$\begin{aligned}
P_R =& \sqrt{\frac{(\hbar^2\Gamma\tau + M)}{4M}} \exp\left(\frac{\hbar^2\Gamma\beta V^\ddagger\tau}{\hbar^2\Gamma\tau + M}\right)\left[\exp\left[\frac{\hbar^2\Gamma\tau(\beta\Delta V)}{(\hbar^2\Gamma\tau + M)}\right]\mathrm{erf}\left(\sqrt{\frac{2M^2(V^\ddagger + \Delta V)}{\hbar^2\Gamma(\hbar^2\Gamma\tau + M)}}\right)\right] \\
&+ \sqrt{\frac{(\hbar^2\Gamma\tau + M)}{4M}} \exp\left(\frac{\hbar^2\Gamma\tau\beta V^\ddagger}{\hbar^2\Gamma\tau + M}\right)\left[\mathrm{erf}\left(\sqrt{\frac{2M^2V^\ddagger}{\hbar^2\Gamma(\hbar^2\Gamma\tau + M)}}\right) + \exp\left(\frac{\hbar^2\Gamma\tau(\beta\Delta V)}{(\hbar^2\Gamma\tau + M)}\right) - 1\right] \\
&+ \frac{\exp(\beta V^\ddagger)}{2}\left[1 - \mathrm{erf}\left(\sqrt{\frac{2MV^\ddagger}{\hbar^2\Gamma}}\right)\right] + \frac{1}{2}\exp[\beta(V^\ddagger + \Delta V)]\left[1 - \mathrm{erf}\left(\sqrt{\frac{2\mathrm{M}(\mathrm{V}^\ddagger + \Delta\mathrm{V})}{\hbar^2\Gamma}}\right)\right]. \qquad (3.6)
\end{aligned}$$

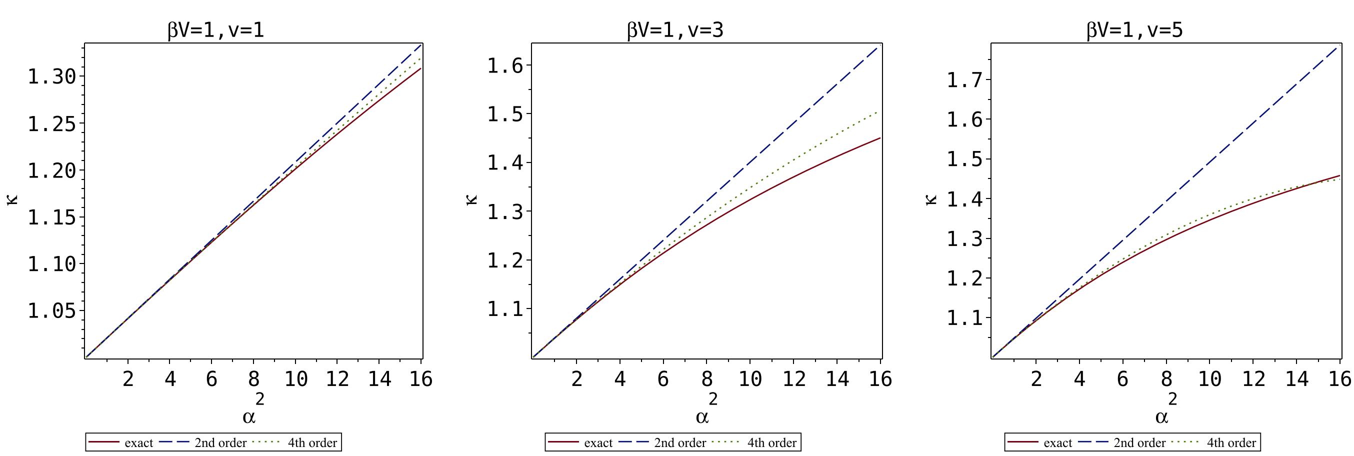

FIG. 2. $\hbar^4$ expansion of the transmission coefficient for the Eckart barrier. In all panels, the solid line is the numerically exact transmission factor, the dotted line is the analytical result including terms up to $\hbar^4$, and the dashed line is the contribution from the analytical result but only including terms up to $\hbar^2$. In all three panels the reduced barrier height is 1 while the asymmetry parameter $v = v_2/v_1$ varies from unity (symmetric potential) to 3 to 5 as one goes from left to right.

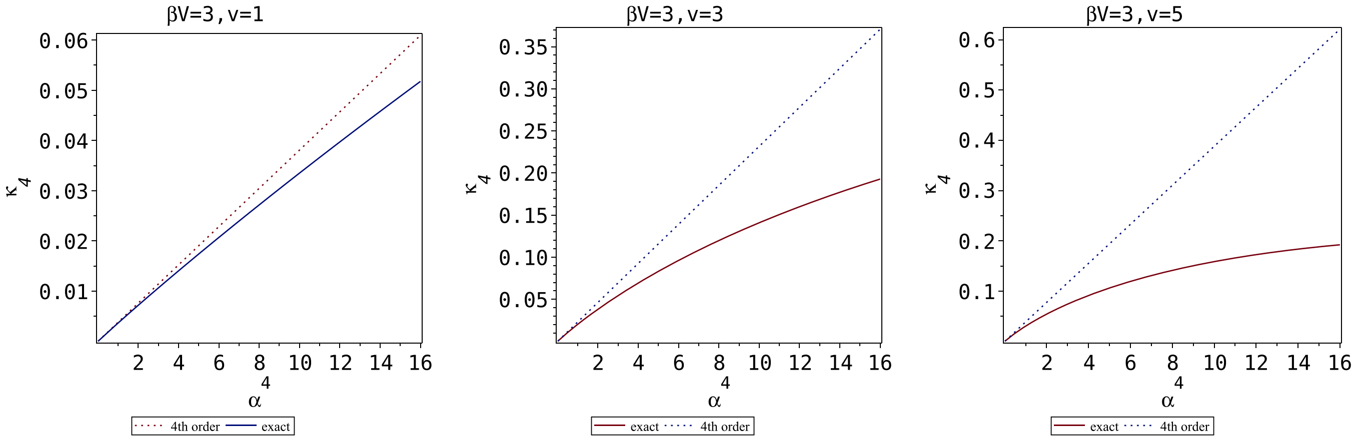

FIG. 3. $\hbar^4$ dependence of the residue of the numerically exact transmission factor when the zeroth-order and $\hbar^2$ terms are subtracted from it. In all panels, the solid line is the numerically exact residue $\Delta\kappa_4$ while the dotted line is the analytical result for κ_4. In all three panels the reduced barrier height is 3 while the asymmetry parameter $v = \frac{v_2}{v_1}$ varies from unity (symmetric potential) to 3 to 5 as one goes from left to right.

In this expression, $\tau = \beta/2$ and ΔV is the exoergicity of the potential. The challenge is to determine the width parameter Γ whose origin is in the coherent-state basis set used in the flux side expression. It was this challenge that motivated in part the present derivation of κ_2 and κ_4. The expression P_R may be expanded as a series in $\hbar^2$ and one finds [16]

$$P_R = 1 + \frac{\hbar^2\Gamma\beta}{2M}\left(\frac{1}{2} + \beta(V^\ddagger + \Delta V)\right) + \frac{\hbar^4\Gamma^2\beta^2}{8M^2}\left[(\beta(V^\ddagger + \Delta V))^2 - (\beta(V^\ddagger + \Delta V)) - \frac{1}{4}\right] + O(\hbar^6). \tag{3.7}$$

One may then also expand the width parameter in terms of $\hbar^2$ as

$$\Gamma = \Gamma_0 + \hbar^2\Gamma_1 \tag{3.8}$$

and derive the relevant expressions for the coefficients Γ_0 and Γ_1 from the known expressions for κ_2 and κ_4 given in Eqs. (1.1) and (2.41):

$$\Gamma_0 = \frac{2M\kappa_2}{\hbar^2\beta\left(\frac{1}{2} + \beta(V^\ddagger + \Delta V)\right)}, \tag{3.9}$$

$$\Gamma_1 = \frac{2M\kappa_4}{\hbar^4\beta\left(\frac{1}{2} + \beta(V^\ddagger + \Delta V)\right)} - \frac{M\kappa_2^2\left[(\beta(V^\ddagger + \Delta V))^2 - (\beta(V^\ddagger + \Delta V)) - \frac{1}{4}\right]}{\hbar^4\beta\left(\frac{1}{2} + \beta(V^\ddagger + \Delta V)\right)^3}. \tag{3.10}$$

These are then inserted into Eq. (3.6) to obtain an approximate expression for the transmission coefficient which is exact to order $\hbar^4$.

To see how good this estimate is, we applied it to the two "standard" Eckart models used as benchmarks for many approximate theories. The symmetric Eckart barrier case is defined by $\alpha = \pi/3$ and $d = 2$. The results are shown in Fig. 5 where we plot in the right panel the ratio of the ex-

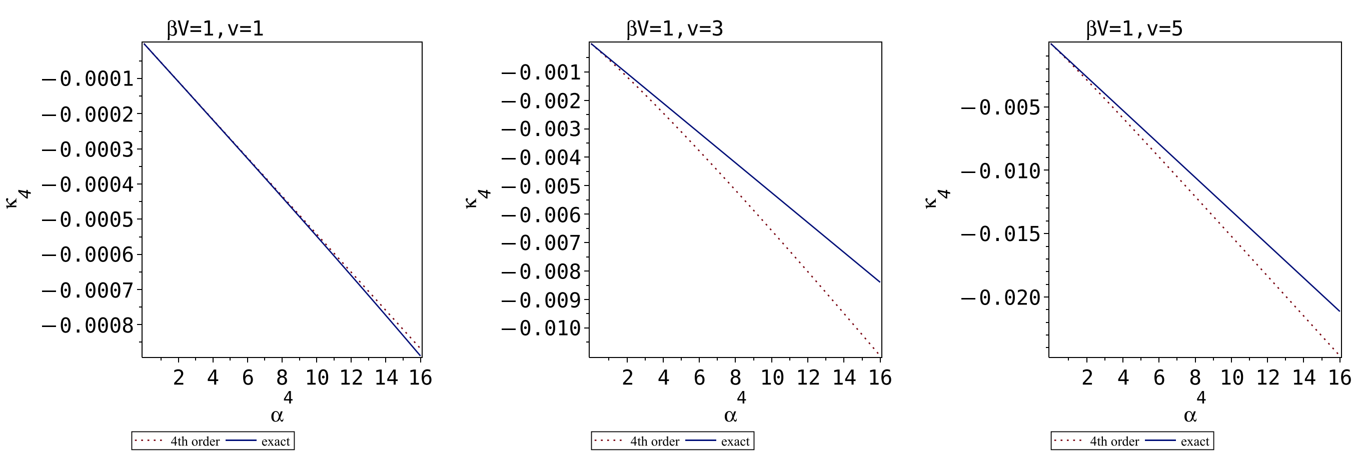

FIG. 4. $\hbar^4$ dependence of the residue of the numerically exact transmission factor when the zeroth-order and $\hbar^2$ terms are subtracted from it. In all panels, the solid line is the numerically exact residue $\Delta\kappa_4$ while the dotted line is the analytical result for κ_4. In all three panels the reduced barrier height is 1 while the asymmetry parameter $v = \frac{v_2}{v_1}$ varies from unity (symmetric potential) to 3 to 5 as one goes from left to right.

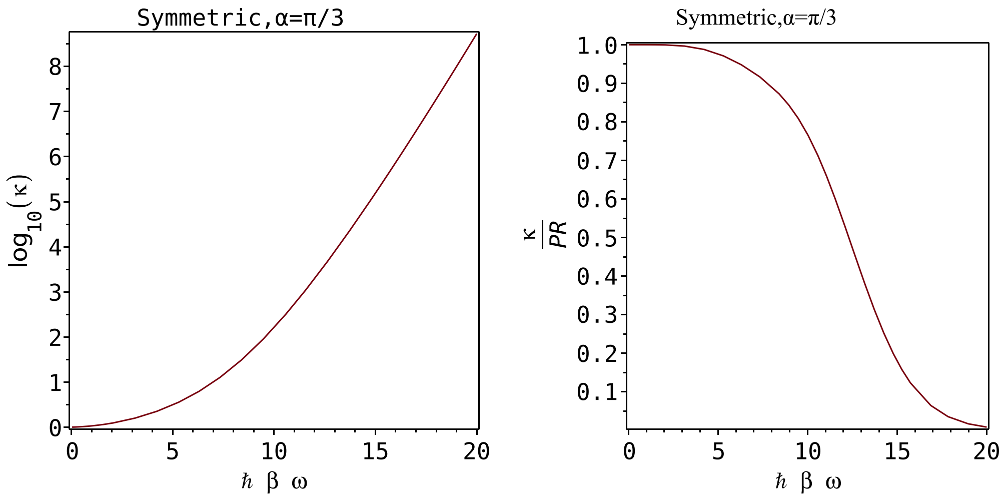

FIG. 5. Ratio of the exact transmission factor to the thawed Gaussian estimate for a symmetric Eckart barrier. The left panel (a) shows the numerically exact transmission factor as a function of the reduced inverse temperature ($\hbar\beta\omega$) while the right panel (b) shows the ratio. One notes that the thawed Gaussian expression significantly extends the range of low temperatures for which the approximate theory is within a factor of 2 of the exact result. The ordinate shows the logarithm base 10 of the transmission factor.

act transmission factor to the approximate one as a function of the inverse temperature and compare with the exact rate which is shown on the left panel. Note that the approximate result is within a factor of 2 as compared to the exact one for $\hbar\beta\omega \lesssim 12$ and that the transmission factor varies over four orders of magnitude in this range. The asymmetric case ($\alpha = 3\pi/16, d = 1$) is shown in Fig. 6. In this case, the approximate expression is within a factor of 2 of the exact result for $\hbar\beta\omega \lesssim 10$ and the transmission factor varies over a range of two orders of magnitude. As is well known, the asymmetric case is more difficult to fit with an approximate theory. These results may be further improved by using a logarithmic combination of the width parameters as in Eq. (3.27) of Ref. [16]. The fitting of the temperature dependence of the width parameter then becomes a prime candidate for machine learning. The width parameter would become a function of the potential parameters and the inverse temperature, fitted to give the exact transmission probability over the whole range of temperatures.

C. The tanh barrier

We assume the following potential barrier:

$$V(x; x_0, V_0) = \frac{V_0}{2\tanh\left(\frac{x_0}{d}\right)}\left[\tanh\left(\frac{x+x_0}{d}\right) - \tanh\left(\frac{x-x_0}{d}\right)\right] \tag{3.11}$$

TABLE I. Numerical verification of the accuracy of the $\hbar^4$ term.

βV_1	v	α	$\frac{\Delta\kappa}{\alpha^4}$	$\frac{\kappa_4}{\alpha^4}$
3	1	0.04	0.0038084	0.0038086
3	3	0.04	0.023171	0.023175
3	5	0.04	0.038793	0.038805
1	1	0.04	−0.00005423	−0.00005425
1	3	0.04	−0.00052474	−0.00052465
1	5	0.04	−0.0013222	−0.0013213

where V_0 is the barrier height and d is a length scale. As shown in Fig. 7 (using $d = 1$) the form of the potential depends critically on the length parameter x_0. In the limit that $x_0 \to 0$ the potential reduces to a symmetric Eckart barrier. In the limit that x_0 is sufficiently large the potential tends to a step potential whose width is $2x_0$. The derivatives of the potential at the barrier top ($x = 0$) are found to be

$$V_2(x_0, V_0) \equiv \left.\frac{\partial^2 V(x; x_0, V_0)}{\partial x^2}\right|_{x=0} = -\frac{2V_0}{d^2\cosh^2\left(\frac{x_0}{d}\right)}, \tag{3.12}$$

$$V_4(x_0, V_0) \equiv \left.\frac{\partial^4 V(x; x_0, V_0)}{\partial x^4}\right|_{x=0} = \frac{8V_0\left[3-\cosh^2\left(\frac{x_0}{d}\right)\right]}{d^4\cosh^4\left(\frac{x_0}{d}\right)}. \tag{3.13}$$

This implies that the second derivative is always negative but the fourth derivative turns from positive to negative when $3 = \cosh^2(\frac{x_0}{d})$. Furthermore, the ratio of the fourth to the second derivative

$$\frac{V_4(x_0, V_0)}{V_2(x_0, V_0)} = -\frac{4}{d^2\cosh^2\left(\frac{x_0}{d}\right)}\left[3-\cosh^2\left(\frac{x_0}{d}\right)\right] \tag{3.14}$$

remains finite for any value of x_0 even though the second derivative vanishes when $x_0 \to \infty$. One finds that

$$\kappa_2(x_0, V_0, \beta, d) = \frac{\hbar^2\beta\left[3+2\beta V_0-\cosh^2\left(\frac{x_0}{d}\right)\right]}{24d^2M\cosh^2\left(\frac{x_0}{d}\right)} \tag{3.15}$$

and

$$\lim_{x_0\to\infty}\kappa_2(x_0, V_0, \beta, d) = -\frac{\hbar^2\beta}{24d^2M} \tag{3.16}$$

while

$$\lim_{x_0\to 0}\kappa_2(x_0, V_0, \beta, d) = \frac{\hbar^2\beta^2\omega^2}{24}\left(1+\frac{1}{\beta V_0}\right) \tag{3.17}$$

and, as expected, this is identical to the Eckart barrier result.

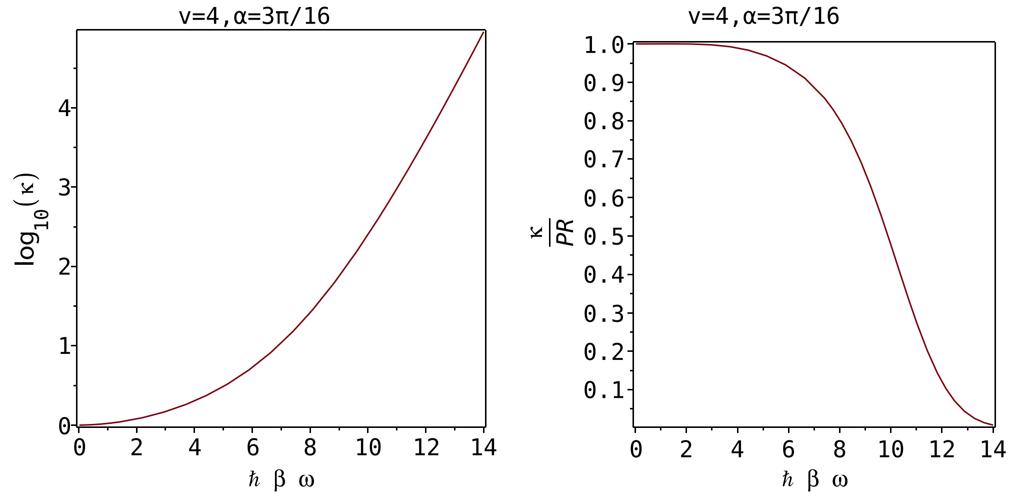

FIG. 6. Ratio of the exact transmission factor to the thawed Gaussian estimate for an asymmetric Eckart barrier. The left panel (a) shows the numerically exact transmission factor as a function of the reduced inverse temperature ($\hbar\beta\omega$) while the right panel (b) shows the ratio. One notes that the thawed Gaussian expression significantly extends the range of low temperatures for which the approximate theory is within a factor of 2 of the exact result. The ordinate shows the logarithm base 10 of the transmission factor.

Similarly one finds that

$$\kappa_4(x_0, V_0, \beta, d) = \frac{\hbar^4\beta^2\left[21\beta V_0\cosh^4\left(\frac{x_0}{d}\right) + 6\left(2\beta^2V_0^2 + 15\beta V_0 + 45\right)\sinh^2\left(\frac{x_0}{d}\right) + \beta V_0\left(28\beta^2V_0^2 - 24\beta V_0 - 45\right)\right]}{10\times 24^2M^2d^4\beta V_0\cosh^4\left(\frac{x_0}{d}\right)} \tag{3.18}$$

so that in the limit of a thick barrier

$$\lim_{x_0\to\infty}\kappa_4(x_0, V_0, \beta, d) = \frac{7\hbar^4\beta^2}{30\times 64M^2d^4} \tag{3.19}$$

and the $\hbar^4$ contribution is positive. We also note that in the limit that $x_0 \to 0$ Eq. (3.18) reduces to the result of the Eckart barrier.

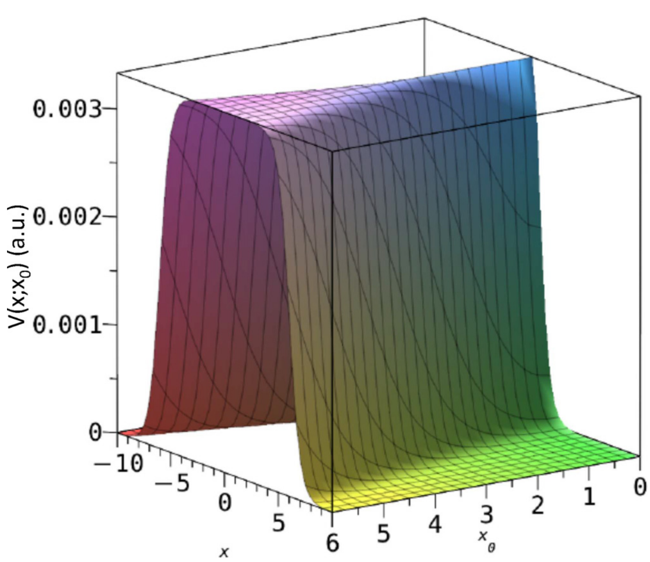

FIG. 7. The tanh potential given in Eq. (3.11). Note that the barrier height is the same for all values of the scale parameter x_0. Both length scales are in atomic units. The ordinate is also in atomic units, denoted as (a.u.).

As an example we consider an approximate hydrogen atom mass ($M = 2000$ a.u.), a range of unity ($d = 1$ a.u.), and a barrier height $V_0 = 1/300$ a.u. We choose the range of temperature going from $T = 200$ to 1000 K which in atomic units leads to $\approx 300 \leqslant \beta \leqslant 1500$ so that $1 \leqslant \beta V_0 \leqslant 5$. In Fig. 7 we first plot the potential as a function of x and x_0. For small x_0 the potential is parabolic in nature while for large x_0 it goes to a broad square barrier. In Fig. 8(a) we plot the second-order (κ_2) contributions to the rate for three different inverse temperatures ($\beta V_0 = 1, 5/3, 5$) as a function of x_0, and the same is shown in Fig. 8(b) for the fourth-order contribution (κ_4). We note that in all cases the fourth-order contribution is substantially smaller than the second-order contribution, implying that the sum of the two would give a true reflection of the rate for the chosen parameter region.

Second, we notice that for $x_0 \lesssim 1.5$ the $\hbar^2$ contribution is positive; in this region, the second derivative gives the dominant effect, and tunneling increases the rate as for the Eckart barrier. However, for larger values, the fourth-order derivative changes sign and the contribution turns negative implying that above barrier reflection is the dominant contribution, and it decreases the rate. In contrast the $\hbar^4$ contribution is negative only for small values of x_0 and only at low temperature. However, due to the fact that the contribution is small it does not significantly change the overall rate. In Fig. 9 we plot the full transmission coefficient $(1 + \kappa_2 + \kappa_4)$ as a function of x_0 and the same three temperatures as in the previous figures. One notices that if the barrier is broad enough the transmission coefficient is less than unity, exemplifying the importance of quantum reflection even when considering thermal rates. The negative contribution for large values of x_0 reflects the fact

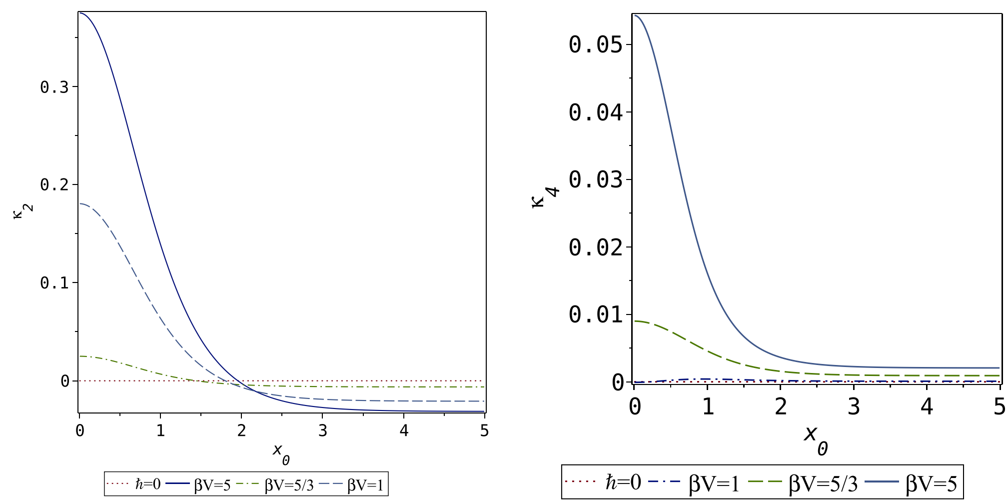

FIG. 8. Second- (left panel) and fourth-order (right panel) contributions to the transmission coefficient of the tanh potential given in Eqs. (3.15) and (3.18), respectively.

that for the quartic barrier the transmission coefficient is, up to fourth order in $\hbar$, less than unity.

IV. DISCUSSION

The main theme of this paper was the derivation of the exact fourth-order-in-$\hbar$ correction to the transmission coefficient of a particle scattered on a one-dimensional barrier potential. The methodology used to derive the expression was based on the Wigner phase-space representation of the exact flux-side expression for the rate. It may be readily extended to higher orders beyond $\hbar^4$ although it is clear that this would involve expanding the potential at the barrier to even higher order than the eighth derivative needed for the $\hbar^4$ term. Obtaining the exact expansion serves as a benchmark for approximate theories. Here, we found out that the semiclassical fourth-order vibrational perturbation theory (VPT-4) of Ref. [19] cannot reproduce the correct $\hbar^4$ expansion. This is also a failure of all other approximate theories such as Wigner dynamics, centroid molecular dynamics (CMD), and ring polymer molecular dynamics.

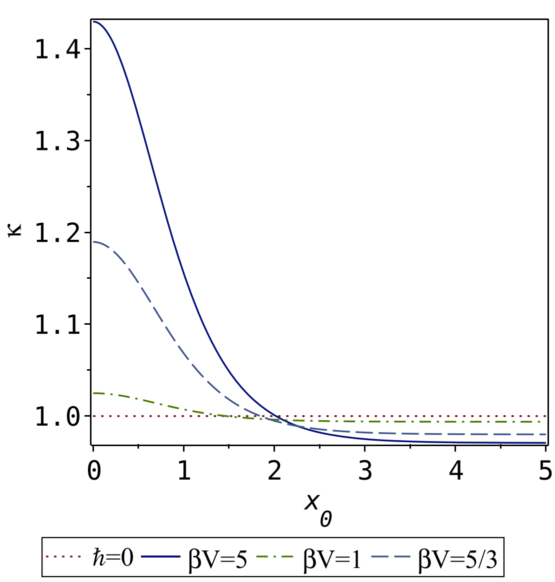

FIG. 9. The transmission coefficient ($\kappa = 1 + \kappa_2 + \kappa_4$) for the tanh potential given in Eq. (3.11) is plotted as a function of the distance x_0 which determines the shape of the potential.

Furthermore, the methodology sheds light on the intriguing case when the second derivative vanishes, a difficulty that already bothered Wigner in 1932 [1]. We showed that the $\hbar^2$ term of the transmission coefficient vanishes while the $\hbar^4$ term is negative, implying that here the dominant quantum effect is quantum above barrier reflection rather than quantum tunneling. This is a result of the increasing width of the barrier, which leads to above barrier reflection. We exemplified this also for a tanh barrier with varying width. When sufficiently large, even though the second derivative at the barrier is always negative, the leading-order contribution to the thermal rate becomes negative, exemplifying the importance of quantum reflection in such cases. Furthermore, in this case, the ratio of the fourth-order derivative at the barrier to the second-order derivative remains finite even in the limit that the second-order derivative vanishes. The same occurs for the Eckart barrier, indicating that for normal potential functions there is no real difficulty in this limit.

Perhaps the most important next challenge is to repeat the derivations presented here for multidimensional systems. The main difficulty is that in such cases the classical projection operator is strictly speaking not known analytically, as coupling between the reaction coordinate and additional degrees of freedom leads to recrossing of the barrier dividing surface. The same would happen when considering the rate for dissipative systems, where the coupling to the bath will lead to recrossing. However, one could carry out at least in principle a perturbation theory where the small term would be the coupling between the reaction coordinate and other degrees of freedom since in the separable case the projection operator is known exactly. A theory for the $\hbar^2$ expansions of the projection operator has been presented in Ref. [22] and should then be applicable in a straightforward but perhaps not trivial way to obtain the leading orders in the expansion of the transmission coefficient in powers of $\hbar^2$. Apart from the intellectual challenge of deriving such an expansion, it would be especially timely in view of recent applications of machine learning toward the prediction of thermal rate constants [15,24–27]. The exact expansion would serve as critical input for such an approach.

An alternative route for deriving quantum corrections in open quantum systems [28] is the cumulant expansion of the semiclassical transition state theory rate calculation which has been shown in Ref. [5] to agree with the exact quantum calculation to order $\hbar^2$. A similar $\hbar$ expansion was carried out for vibrational response theory in the action angle variable representation, leading to competition between anharmonicity and dissipation [29]. Along the same line, the effect of this competition on quantum transmission will be explored in future work.

ACKNOWLEDGMENTS

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APPENDIX A: DERIVATION OF THE EXPRESSION FOR κ_{42}

To obtain an expression for the $\hbar^4$ correction to the projection operator we follow the same route as in Ref. [5]. First we note that for any function $f(p,q)$ which multiplies a derivative of the Dirac delta function $\delta[p-g(q)]$ we have the following relations:

$$\delta' f = f[g(q),q]\delta' - f'[g(q),q]\delta, \tag{A1}$$

$$\delta'' f = f[g(q),q]\delta'' - 2f'[g(q),q]\delta' + f''[g(q),q]\delta, \tag{A2}$$

$$\delta^{(3)} f = f[g(q),q]\delta^{(3)} - 3f'[g(q),q]\delta'' + 3f''[g(q),q]\delta' - f^{(3)}[g(q),q]\delta, \tag{A3}$$

$$\delta^{(4)} f = f(g(q),q)\delta^{(4)} - 4f'[g(q),q]\delta^{(3)} + 6f''[g(q),q]\delta'' - 4f^{(3)}[g(q),q]\delta' + f^{(4)}(g(q),q)\delta, \tag{A4}$$

$$\delta^{(5)} f = f(g(q),q)\delta^{(5)} - 5f'[g(q),q]\delta^{(4)} + 10f''[g(q),q]\delta^{(3)} - 10f^{(3)}[g(q),q]\delta'' + 5f^{(4)}(g(q),q)\delta' - f^{(5)}(g(q),q)\delta. \tag{A5}$$

The primes and superscripts in parentheses denote partial differentiation with respect to the momentum.

The equation which determines $P_2(p,q)$ is derived from Eq. (3.27) of Ref. [22] as adapted to the $\hbar^4$ term:

$$\frac{dP_2(p_t,q_t)}{dt} = \dot{p}_{sx}(t)\frac{\partial P_2(p_{q_t},q_t)}{\partial p_{q_t}} + \frac{p_{q_t}}{M}\frac{\partial P_2(p_{q_t},q_t)}{\partial q_t} = \frac{dV_1(q_t)}{dq_t}\frac{\partial P_2(p_{q_t},q_t)}{\partial p_{q_t}} - \frac{1}{24}\frac{d^3V_1(q_t)}{dq_t^3}\frac{\partial^3 P_1(p_{q_t},q_t)}{\partial p_{q_t}^3} + \frac{1}{16\times 120}\frac{d^5V_1(q_t)}{dq_t^5}\frac{\partial^5 P_0(p_{q_t},q_t)}{\partial p_{q_t}^5} \tag{A6}$$

with p_{sx} as defined in Eq. (2.31) and $V_1(q_t)$ the nonlinear part of the potential:

$$V_1(q) = V(q) - \tfrac{1}{2}V_2 q^2. \tag{A7}$$

Notice that by definition [Eq. (3.21) of [22]]

$$\dot{p}_{sx}(t) - \frac{dV_1(x_t)}{dx_t} = M\omega^2 x_t - \frac{p_x(t)V'(x_t)}{\sqrt{-2MV(x_t)}} - \frac{dV_1(x_t)}{dx_t} = -\frac{p_{sx}(t)V'(x_t)}{\sqrt{-2MV(x_t)}}. \tag{A8}$$

We then notice from Eqs. (2.16) and (2.17) that the second and third terms on the right-hand side of Eq. (A6) involve the delta function derivatives $\delta^{(j)}(p_{sx})$ with j going from 3 to 5, that is,

$$\frac{\partial^3 P_1(p_t,q_t)}{\partial p_t^3} = \sum_{j=0}^{2} g_{j1}(q_t)\delta^{(j+3)}[p_{sx}(t)] \tag{A9}$$

and

$$\frac{\partial^5 P_0(p_t,q_t)}{\partial p_t^5} = \delta^{(4)}[p_{sx}(t)]. \tag{A10}$$

Using Eq. (A9) we rewrite Eq. (A6) as

$$-\frac{p_{sx}(t)V'(q_t)}{\sqrt{-2MV(q_t)}}\frac{\partial P_2(p_t,q_t)}{\partial p_t} = -\frac{p_{q_t}}{M}\frac{\partial P_2(p_{q_t},q_t)}{\partial q_t} - \frac{1}{24}\frac{d^3V_1(q_t)}{dq_t^3}\frac{\partial^3 P_1(p_{q_t},q_t)}{\partial p_{q_t}^3} + \frac{1}{16\times 120}\frac{d^5V_1(q_t)}{dq_t^5}\frac{\partial^5 P_0(p_{q_t},q_t)}{\partial p_{q_t}^5}. \tag{A11}$$

From the identities given in Eqs. (A1)–(A5) and (2.30) this may be rewritten as

$$\frac{V'(q)}{\sqrt{-2MV(q)}}\sum_{j=0}^{\infty}(j+1)g_{j2}(q)\delta^{(j)}(p_{sx}) = \frac{\sqrt{-2MV(q_t)}}{M}\sum_{j=0}^{\infty}g'_{j2}(q)\delta^{(j)}(p_{sx}) + \frac{1}{M}\sum_{j=0}^{\infty}jg'_{j2}(q)\delta^{(j-1)}(p_{sx}) - \frac{1}{24}\frac{d^3V(q)}{dq^3}\sum_{j=0}^{2}g_{j1}(q)\delta^{(j+3)}(p_{sx}) + \frac{1}{16\times 120}\frac{d^5V(q)}{dq^5}\delta^{(4)}(p_{sx}). \tag{A12}$$

Demanding that the coefficients of the derivatives of $\delta^{(n)}(p_{sx})$ with $n = 0, 1, \dots, 5$ vanish gives the six differential equations

$$\frac{dg_{52}(q)}{dq} = -3\frac{V'(q)}{V(q)}g_{52}(q) - \frac{M}{2\times 24^2}V^{(3)}(q)\left(\frac{V''(q)}{V(q)} - \frac{[V'(q)]^2}{2[V(q)]^2}\right), \tag{A13}$$

$$\frac{dg_{42}(q)}{dq} = -\frac{5V'(q)}{2V(q)}g_{42}(q) + \frac{M}{24\sqrt{-2MV(q)}}V^{(3)}(q)g_{11}(q) - \frac{M}{16\times 120\sqrt{-2MV(q)}}V^{(5)}(q) - \frac{5}{\sqrt{-2MV(q)}}\frac{dg_{52}(q)}{dq}, \tag{A14}$$

$$\frac{dg_{32}(q)}{dq} = -\frac{2V'(q)}{V(q)}g_{32}(q) + \frac{M}{24\sqrt{-2MV(q)}}V^{(3)}(q)g_{01}(q) - \frac{4}{\sqrt{-2MV(q)}}\frac{dg_{42}(q)}{dq}, \tag{A15}$$

$$\frac{dg_{22}(q)}{dq} = -\frac{3V'(q)}{2V(q)}g_{22}(q) - \frac{3}{\sqrt{-2MV(q)}}g'_{32}(q), \tag{A16}$$

$$\frac{dg_{12}(q)}{dq} = -\frac{V'(q)}{V(q)}g_{12}(q) - \frac{2}{\sqrt{-2MV(q)}}g'_{22}(q), \tag{A17}$$

$$\frac{dg_{02}(q)}{dq} = -\frac{V'(q)}{2V(q)}g_{02}(q) - \frac{g'_{12}(q)}{\sqrt{-2MV(q)}}. \tag{A18}$$

These equations have to be solved, such that there are no divergences and each of the functions is finite when $q \to 0$. With some straightforward algebra we find the following solutions:

$$g_{52}(q) = -\frac{M}{4\times 24^2 V(q)}\left(\frac{[V'(q)]^2}{2V(q)} - V''(q)\right)^2, \tag{A19}$$

$$\begin{aligned} g_{42}(q) = &-\frac{\sqrt{M}}{24^2\sqrt{-2V(q)}}\left\{\frac{13V'^2(q)V''(q)}{5V^2(q)} - \frac{29V''^2(q)}{20V(q)} - \frac{V_2}{2}\left[\frac{V''(q)}{V(q)} - \frac{V'^2(q)}{2V^2(q)}\right]\right\} \\ &+\frac{\sqrt{M}}{24^2\sqrt{-2V(q)}}\left\{\frac{15V'^4(q)}{16V^3(q)} - \frac{3}{10}\left[V^{(4)}(q) - \frac{2V^{(3)}(q)V'(q)}{V(q)}\right]\right\}, \end{aligned} \tag{A20}$$

$$\begin{aligned} g_{32}(q) = &-\frac{g_{11}(0)}{24\times 2}\left[\frac{V(q)V''(q)}{V^2(q)} - \frac{V'^2(q)}{2V^2(q)}\right] - \frac{1}{24^2V^2(q)}\left\{\frac{59V'^2(q)V''(q)}{8V(q)} - \frac{27V''^2(q)}{10} - \frac{5V_2}{4}\left(V''(q) - \frac{V'^2(q)}{V(q)}\right)\right\} \\ &+\frac{1}{24^2V^2(q)}\left\{\frac{105V'^4(q)}{32V^2(q)} - \frac{3V(q)V^{(4)}(q)}{5} + \frac{21V'(q)V^{(3)}(q)}{10}\right\}, \end{aligned} \tag{A21}$$

$$g_{22}(q) = -\frac{3}{\sqrt{-2MV(q)}}\left[g_{32}(q) + \frac{g_{11}(0)}{24\times 2V(q)}\left(\frac{V'^2(q)}{2V(q)} - V_2\right) + \frac{K_2(q) - K_2(0)}{24^2V(q)}\right], \tag{A22}$$

where we used the notation

$$K_2(q) = \frac{1}{V(q)}\left(\frac{35V'^4(q)}{32V^2(q)} - \frac{V'^2(q)(12V''(q) + 5V_2)}{8V(q)} - \frac{3V''^2(q)}{10} + \frac{7V_2^2}{40} + \frac{3V'(q)V^{(3)}(q)}{5}\right) \tag{A23}$$

and note that

$$K_2(0) \equiv \lim_{q\to 0} K_2(q) = \frac{25V_3^2 - 27V_2V_4}{180V_2}. \tag{A24}$$

Also

$$g_{12}(q) = \frac{9}{48MV(q)}\left[\frac{g_{11}(0)}{4}\left(\frac{2V_2}{V(q)} - \frac{V'^2(q)}{V^2(q)}\right) + \frac{K_2(0) - K_2(q)}{24V(q)}\right] - \frac{1}{V(q)}\left(\frac{3}{M}g_{32}(q) - K_1\right) \tag{A25}$$

with

$$K_1 \equiv \frac{216V_2^3V_6 - 552V_2^2V_3V_5 - 405V_2^2V_4^2 + 870V_2V_3^2V_4 - 245V_3^4}{1\,658\,880V_2^4}. \tag{A26}$$

The $q = 0$ limits of Eqs. (A19), (A21), and (A25) are then given as in Eqs. (2.33)–(2.35), respectively. There is no need to solve for $g_{02}(q)$ since it does not contribute to the rate.

APPENDIX B: DERIVATION OF THE EXPRESSION FOR κ_{44}

Obtaining this term is quite tedious, so we give it in some detail. In addition to Eqs. (2.22) and (2.24) we note the following limits for the spatial coefficients appearing in the expression for $P_1(p,q)$:

$$g'_{21}(0) = \frac{9V_2V_4 - V_3^2}{864\omega V_2}, \tag{B1}$$

$$\frac{V_3}{3\omega} = \lim_{q\to 0}\frac{d}{dq}\left[\frac{MV'(q)}{\sqrt{-2MV(q)}}\right] = \lim_{q\to 0}\frac{1}{\omega q}\left(V''(q) - \frac{V'^2(q)}{2V(q)}\right), \tag{B2}$$

$$-M\omega = \lim_{q\to 0}\left[\frac{MV'(q)}{\sqrt{-2MV(q)}}\right], \tag{B3}$$

as well as the following momentum integrals:

$$\int_{-\infty}^{\infty} dp\frac{p}{M}\delta'''(p)\left[1 - \frac{\beta p^2}{M}\right]\exp\left(-\frac{\beta p^2}{2M}\right) = \frac{9\beta}{M^2}, \tag{B4}$$

$$\int_{-\infty}^{\infty} dp\frac{p}{M}\delta'(p)\left[1 - \frac{\beta p^2}{M}\right]\exp\left(-\frac{\beta p^2}{2M}\right) = -\frac{1}{M}. \tag{B5}$$

The definition of κ_{44} as obtained from Eq. (2.27) is such that it can be separated into two terms:

$$\begin{aligned}\kappa_{44} &= -\frac{\hbar^4\beta}{8}\int_{-\infty}^{\infty} dpdq\left[\frac{p}{M}\delta(q)\hat{\Lambda}^2\Omega_0(p,q;\beta)\right]P_1(p,q)\\ &= -\frac{\hbar^4\beta^2}{8M}\int_{-\infty}^{\infty} dpdq\frac{p}{M}\delta(q)\left(3 - \frac{\beta p^2}{M}\right)\\ &\quad\times \beta V''(q)\Omega_0(p,q;\beta)P_1(p,q)\\ &\quad+ \frac{\hbar^4\beta^2}{8M}\int_{-\infty}^{\infty} dpdq\frac{p}{M}\delta(q)\left(1 - \frac{\beta p^2}{M}\right)\Omega_0(p,q;\beta)\\ &\quad\times \frac{\partial^2 P_1(p,q)}{\partial q^2}\\ &\equiv \kappa_{441} + \kappa_{442}.\end{aligned} \tag{B6}$$

The first integral is relatively straightforward involving two integrations by parts over the momentum variable:

$$\kappa_{441} = \frac{\hbar^4\beta^4\omega^4}{16\times 16}\left(\frac{V_4}{\beta V_2^2} - \frac{V_3^2}{3\beta V_2^3}\right). \tag{B7}$$

The second integral is more involved due to the differentiation of the coefficients $g_{j1}(q)$ but is also rather straightforward and one finds

$$\begin{aligned}\kappa_{442} &= \frac{9\hbar^4\beta^3}{8M^2}[2\omega g'_{21}(0) + M\omega^2 g_{11}(0)]\\ &= \frac{\hbar^4\beta^3}{256M^2}\left(3V_4 + \frac{V_3^2}{3V_2}\right).\end{aligned} \tag{B8}$$

Summing the two terms leads to Eq. (2.38).

APPENDIX C: DERIVATION OF THE EXPRESSION FOR κ_{45}

As in the case of the expression for κ_{44} detailed in the previous Appendix, the expression for κ_{45} may be divided into two parts:

$$\begin{aligned}\kappa_{45} &= \frac{\beta\hbar^4}{4}\int_{-\infty}^{\infty} dpdq\left[\frac{1}{M}\delta'(q)\frac{\partial^2}{\partial p\partial q}\Omega_1(p,q;\beta)\right]P_0(p,q)\\ &\quad-\frac{\beta\hbar^4}{8}\int_{-\infty}^{\infty} dpdq\left[\frac{p}{M}\delta''(q)\frac{\partial^2}{\partial p^2}\Omega_1(p,q;\beta)\right]P_0(p,q)\\ &= \kappa_{451} + \kappa_{452}.\end{aligned} \tag{C1}$$

Using the explicit expression for the first-order-in-$\hbar^2$ expression for the thermal density [Eq. (2.13)] one readily finds that

$$\kappa_{451} = \frac{5\beta^4\hbar^4\omega^4}{96} - \frac{3\beta^4\hbar^4\omega^4}{96}\frac{V_4}{\beta V_2^2}. \tag{C2}$$

The second term is slightly more involved due to the second derivative of the spatial delta function which implies an additional integration by parts, however it too is straightforward and one finds

$$\kappa_{451} = \frac{\beta^4\hbar^4\omega^4}{64}\left(\frac{V_4}{\beta V_2^2}\right) - \frac{5\beta^4\hbar^4\omega^4}{96} \tag{C3}$$

so that as given in Eq. (2.39) one obtains

$$\kappa_{45} = \kappa_{451} + \kappa_{452} = -\frac{\beta^4\hbar^4\omega^4}{64}\left(\frac{V_4}{\beta V_2^2}\right) = -\kappa_{44}. \tag{C4}$$

APPENDIX D: AN ERROR IN THE SEMICLASSICAL VPT4 THEORY

In the VPT4 version of the semiclassical theory the energy is expanded in terms of the action as

$$E(\phi) = V_0 + G - W\frac{\phi}{\pi} - X\frac{\phi^2}{\pi^2} + Y\frac{\phi^3}{\pi^3}. \tag{D1}$$

At high energy, if $Y < 0$ the action ϕ goes to minus infinity and the transmission coefficient goes to unity. However, if $Y > 0$, the action would have to go to plus infinity in the high-energy limit and considering Eq. (2.43) this would lead to a vanishing transmission coefficient at high energy. In Ref. [19] the expression given for the coefficient Y is

$$Y = \frac{\omega^3(288\sinh^2\mu - 5670\sinh^4\mu)}{576V^{\ddagger 2}} \tag{D2}$$

where μ is an asymmetry parameter describing the potential, which vanishes when the potential is symmetric. For small asymmetry, the $\sinh^2\mu$ term will dominate, the parameter Y will be positive, and the wrong limit is obtained.

The error comes from truncating the expansion in Eq. (D1) to third order in the action. Extending to fourth order, i.e., VPT-6, would not only prevent the possibility of obtaining the wrong high-energy limit, but would also contribute to the $\hbar^4$ term in the expansion, most probably leading to the exact result derived here. Of course, the price to be paid for such an extension is not only in the extension of the perturbation theory to one higher order, but also to the need of computing at least the sixth and seventh derivatives of the potential at the barrier and this would be computationally costly when considering realistic molecular systems.

APPENDIX E: THE QUARTIC BARRIER

1. Order $\hbar^2$

We assume that the potential has the form

$$V(q) = -\frac{V_4}{24}q^4 \tag{E1}$$

and $V_4 \geqslant 0$. The $\hbar^2$ correction to the thermal density for the quartic barrier is

$$\Omega_1(p,q) = \Omega_0(p,q)\left(\frac{V_4 q^2}{16}\left[\frac{\beta^2}{M} - \frac{\beta^3 p^2}{3M^2}\right] + \frac{\beta^3}{24M}\frac{V_4^2}{36}q^6\right). \tag{E2}$$

The contribution of the term to κ_2 is zero, due to the coordinate dependence of at least order q^2 of the $\hbar^2$ contribution to the density. Similarly, the contribution coming from the Janus operator term vanishes, since the derivatives with respect to the coordinate create a q^3 dependence. The remaining term is the contribution coming from the projection operator. From Eq. (2.17) we know that

$$\begin{aligned}\kappa_{2,P} = \beta \int dpdq \frac{p}{M}\delta(q)\Omega_0(p,q) \\ \times \left[g_{21}(q)\delta''\left(p + \sqrt{\frac{MV_4}{12}}q^2\right)\right. \\ + g_{11}(q)\delta'\left(p + \sqrt{\frac{MV_4}{12}}q^2\right) \\ \left. + g_{01}(q)\delta\left(p + \sqrt{\frac{MV_4}{12}}q^2\right)\right].\end{aligned} \tag{E3}$$

From Eqs. (3.32)– (3.34) of Ref. [22] we know that the equation defining the function $g_{21}(q)$ as applied to the purely quartic barrier is

$$g'_{21}(q) = -6\frac{g_{21}(q)}{q} - \frac{\sqrt{MV_4}}{q\sqrt{48}}. \tag{E4}$$

This has the solution that $g_{21}(q)$ is a constant and one readily finds

$$g_{21}(q) = -\frac{\sqrt{MV_4}}{24\sqrt{3}}. \tag{E5}$$

The equation for g_{11} is

$$-4g_{11}(q)\frac{1}{q} = g'_{11}(q) \tag{E6}$$

so that

$$g_{11}(q) = 0 \tag{E7}$$

and similarly one finds that

$$g_{01}(q) = 0 \tag{E8}$$

so that

$$\kappa_{2,P} = 0. \tag{E9}$$

The second-order-in-$\hbar$ contribution vanishes.

2. Order $\hbar^4$

The derivation of the fourth-order term is a bit lengthier, but remains straightforward.

a. κ_{41}

From Eqs. (2.28) and using the explicit form of the quartic potential [Eq. (E1)] we have that the fourth-order Janus term is

$$\begin{aligned}\kappa_{41} &= \frac{\hbar^4\beta}{16\times 24M}\int_{-\infty}^{\infty} dpdq\left[p\delta^{(4)}(q)\frac{\partial^4\Omega_0(p,q;\beta)}{\partial p^4}\right. \\ &\quad \left. -\frac{2\beta V_4}{3}\delta^{(3)}(q)q^3\frac{\partial^3\Omega_0(p,q;\beta)}{\partial p^3}\right]P_0(p,q) \\ &= \kappa_{411} + \kappa_{412}.\end{aligned} \tag{E10}$$

We then note the identities

$$\begin{aligned}\int_{-\infty}^{\infty} dq\delta^{(4)}(q)\exp\left(\frac{\beta V_4 q^4}{24}\right)\theta\left(p + \sqrt{\frac{MV_4}{12}}q^2\right) \\ = \beta V_4\theta(p) + MV_4\delta'(p),\end{aligned} \tag{E11}$$

$$\int_{-\infty}^{\infty} dq\delta^{(3)}(q)q^3\Omega_0(p,q;\beta)P_0(p,q) = -6\theta(p)\Omega_0(p,0;\beta), \tag{E12}$$

to find that

$$\kappa_{411} = -\frac{\hbar^4}{4\times 24}\frac{\beta^3 V_4}{M^2} \tag{E13}$$

and

$$\kappa_{412} = \frac{\hbar^4}{4\times 24}\frac{\beta^3 V_4}{M^2} \tag{E14}$$

so that

$$\kappa_{41} = 0 \tag{E15}$$

and the term does not contribute just as in the case where there is a parabolic term.

b. κ_{42}

The first differential equation in this case is

$$\frac{dg_{52}(q)}{dq} = -\frac{12}{q}g_{52}(q) + \frac{2M}{24^2}\frac{V_4}{q}. \tag{E16}$$

The solution is that $g_{52}(q)$ is a constant:

$$g_{52}(q) = \frac{MV_4}{6\times 24^2} \tag{E17}$$

and this would also be the result for the quartic barrier as derived from Eq. (A19). One then finds that all the rest of the functions vanish, for example,

$$\frac{dg_{42}(q)}{dq} = -\frac{5V'(q)}{2V(q)}g_{42}(q) \tag{E18}$$

so that

$$g_{42}(q) = 0. \tag{E19}$$

The contribution to the rate from the $\hbar^4$ term of the projection operator is then obtained from Eq. (2.32) adapted to the quartic barrier, to find

$$\kappa_{42} = -\frac{5\hbar^4\beta^4}{2\times 24^2}\frac{V_4}{\beta M^2}. \tag{E20}$$

c. κ_{43}

The $\hbar^4$ contribution to the thermal density at the barrier is given in Eq. (2.14). Adapting it to the quartic barrier potential of Eq. (E1) at $q = 0$ gives

$$\Omega_2(p,0) = \frac{\beta^3 V_4}{15\times 64M^2}\Omega_0(p,0)\left(\frac{\beta^2 p^4}{2M^2} - 5\frac{\beta p^2}{M} + \frac{15}{2}\right). \tag{E21}$$

Its contribution to the transmission coefficient is

$$\kappa_{43} = \frac{1}{10}\frac{\hbar^4\beta^3 V_4}{64M^2} = \frac{9}{10}\frac{\hbar^4\beta^3 V_4}{24^2M^2}. \tag{E22}$$

d. κ_{44} and κ_{45}

The contribution to this case comes from the combination of the Janus operator squared and the $\hbar^2$ term for the projection operator as in Eq. (B6). Adapting it to the quartic barrier gives

$$\kappa_{44} = -\frac{\hbar^4\beta^3 V_4}{64M^2}. \tag{E23}$$

For the quartic barrier we also note that

$$\begin{aligned}&\left[\frac{\beta p}{M}\delta(q)\hat{\Lambda}^2\Omega_1(p,q;\beta)\right]\\ &= \frac{\beta^3 V_4}{16M^2}p\delta''(q)\frac{\partial^2}{\partial p^2}\left[q^2\Omega_0(p,q)\left(1 - \frac{\beta p^2}{3M} + \frac{\beta V_4 q^4}{18\times 3}\right)\right]\\ &\quad -\frac{\beta^3 V_4}{8M^2}\delta'(q)\frac{\partial^2}{\partial q\partial p}\left[q^2\Omega_0(p,q)\left(1 - \frac{\beta p^2}{3M} + \frac{\beta V_4 q^4}{18\times 3}\right)\right]\end{aligned} \tag{E24}$$

so that

$$\kappa_{45} = \frac{\hbar^4\beta^3 V_4}{64M^2} \tag{E25}$$

and, as in the general case, the sum of the two terms ($\kappa_{44} + \kappa_{45}$) vanishes.

e. κ_{46}

This expression involves a product of the $\hbar^2$ correction to the density with the $\hbar^2$ correction to the projection operator. Due to the fact that the first-order-in-$\hbar^4$ contribution to the density vanishes at the barrier, the term κ_{46} also vanishes.

f. Summing it all up

The net result is then that the $\hbar^4$ term for the quartic barrier is

$$\kappa_4 = \kappa_{42} + \kappa_{43} = -\frac{8\hbar^4\beta^3 V_4}{5\times 24^2M^2} \tag{E26}$$

as given also in Eq. (2.47).

APPENDIX F: HEXIC POTENTIAL BARRIER

1. Order $\hbar^2$

We assume that the potential has the form

$$V(q) = -\frac{V_6}{720}q^6 \tag{F1}$$

and $V_6 \geqslant 0$. The $\hbar^2$ correction to the thermal density for the hexic barrier is then

$$\Omega_1(p,q) = \Omega_0(p,q)\left(-\frac{1}{8}\frac{V_6}{24}q^4\left[-\frac{\beta^2}{M} + \left(\frac{\beta^3 p^2}{3M^2}\right)\right] + \frac{\beta^3}{24M}\frac{V_6^2}{120^2}q^{10}\right) \tag{F2}$$

and its contribution to κ_2 vanishes, due to the dependence of at least q^4 which vanishes at the barrier. The second contribution comes from the Janus operator term, but it also vanishes, for the same reason, that is, the coordinate derivatives bring down terms of order q^2 and higher and these vanish at the barrier. The third contribution comes from the projection operator. One readily finds from Eqs. (3.32)– (3.34) of Ref. [22] that

$$g_{21}(q) = -\frac{\sqrt{10MV_6}}{24\times 10}q, \tag{F3}$$

$$g_{11}(q) = \frac{1}{8q^2}, \tag{F4}$$

$$g_{01}(q) = -\frac{3\sqrt{10}}{4\sqrt{MV_6}}\frac{1}{q^5}. \tag{F5}$$

These seemingly divergent results cancel out. When evaluating the relevant term, one must first add up all the terms and only at the end perform the integration over q to find that this contribution also vanishes:

$$\begin{aligned}&\beta\int dpdq\frac{p}{M}\delta(q)\Omega_0(p,q)P_1(p,q)\\ &= \beta\int dpdq\frac{p}{M}\delta(q)\Omega_0(p,q)g_{21}(q)\delta''(p+\sqrt{-2MV(q)})\\ &\quad -\frac{\beta}{M}\int dq\delta(q)g_{11}(q) - \beta^2\int dq\frac{2MV(q)}{M^2}\delta(q)g_{11}(q)\\ &\quad +\frac{\beta}{M}\int dpdq\delta(q)\frac{1}{8}\frac{1}{q^2} = 0.\end{aligned} \tag{F6}$$

The second-order-in-$\hbar$ term does not contribute to the transmission coefficient of the hexic barrier.

2. Order $\hbar^4$

a. κ_{41}

Using Eq. (2.28) and the explicit form of the hexic potential [Eq. (F1)] we have that the fourth-order Janus term is

$$\kappa_{41} = \frac{\hbar^4\beta}{16\times 24M}\int_{-\infty}^{\infty} dpdqp\delta^{(4)}(q)\frac{\partial^4\Omega_0(p,q;\beta)}{\partial p^4}P_0(p,q). \tag{F7}$$

We then note that

$$\int_{-\infty}^{\infty} dq\delta^{(4)}(q)\exp\left(\frac{\beta V_6 q^6}{720}\right)\theta\left(p + \sqrt{\frac{MV_6}{720}}q^3\right) = 0 \tag{F8}$$

since the integration by parts brings down powers of q that vanish at the barrier so that

$$\kappa_{41} = 0. \tag{F9}$$

b. κ_{42}

Showing that this term also vanishes is more involved. The expression is

$$\kappa_{42} = \int dq\delta(q)\sum_{j=0}^{5} g_{j2}(q)I_j(q) \tag{F10}$$

where

$$I_j(q) = \beta\Omega_0(0, q)\int dp\Big[\frac{p}{M}\Omega_0(p, 0)\Big]\delta^{(5)}(p+\sqrt{-2MV(q)})$$
$$= (-1)^j\frac{\beta}{M}\Omega_0(0, q)\int dp\delta(p+\sqrt{-2MV(q)})$$
$$\times\frac{\partial^j}{\partial p^j}[p\Omega_0(p, 0)]. \tag{F11}$$

The functions $g_{j2}(q)$ are readily found to be

$$g_{52}(q) = \frac{MV_6}{24^2}\frac{q^2}{20}, \tag{F12}$$

$$g_{42}(q) = -\frac{\sqrt{10MV_6}}{2\times 960}\frac{1}{q}, \tag{F13}$$

$$g_{32}(q) = \frac{3}{128\times q^4}, \tag{F14}$$

$$g_{22}(q) = \frac{1}{\sqrt{10MV_6}}\frac{5\times 27}{16q^7}, \tag{F15}$$

$$g_{12}(q) = -\frac{3\times 5\times 7\times 27}{16MV_6q^{10}}, \tag{F16}$$

$$g_{02}(q) = \frac{225\times 35\times 27}{2(10MV_6)^{3/2}q^{13}}. \tag{F17}$$

We then find that

$$S(q) \equiv \sum_{j=0}^{5} g_{j2}(q)I_j(q)$$
$$= \frac{MV_6}{24^2}\frac{q^2I_5(q)}{20} - \frac{\sqrt{10MV_6}}{2\times 960}\frac{I_4(q)}{q} + \frac{3I_3(q)}{128\times q^4}$$
$$+\frac{I_2(q)}{\sqrt{10MV_6}}\frac{5\times 27}{16q^7} - \frac{3\times 5\times 7\times 27I_1(q)}{16MV_6q^{10}}$$
$$+\frac{225\times 35\times 27I_0(q)}{2(10MV_6)^{3/2}q^{13}}$$
$$= \frac{MV_6}{24^2}\frac{q^2I_5(q)}{20} - \frac{\sqrt{10MV_6}}{2\times 960}\frac{I_4(q)}{q}$$
$$+q^2\frac{\beta^4V_6^2}{5120\times 1080M^2}q^8 - \frac{1}{32}\frac{\beta^3}{M^2}\frac{V_6}{40}q^2 \tag{F18}$$

and all these terms go as q^n with $n > 0$ so they vanish when integrating over the coordinate. We thus conclude that

$$\kappa_{42} = 0. \tag{F19}$$

c. κ_{43}

The $\hbar^4$ contribution to the thermal density at the barrier is given in Eq. (2.14). Adapting it to the hexic barrier potential of Eq. (F1) gives at most fourth-order derivatives of the potential, so that at $q = 0$ this term too vanishes:

$$\kappa_{43} = 0. \tag{F20}$$

d. κ_{44}

To evaluate this contribution one first sums over all terms and then integrates over the coordinate to find that it vanishes:

$$\kappa_{44} = -\frac{\hbar^4}{8}\int_{-\infty}^{\infty} dpdq\Big[\frac{\beta p}{M}\delta(q)\hat{\Lambda}^2\Omega_0(p, q;\beta)\Big]P_1(p, q)$$
$$= -\frac{\hbar^4}{64}\frac{\beta}{M}\frac{\beta}{M}\int_{-\infty}^{\infty} dq\delta''(q)\frac{1}{q^2}\Omega_0(p, q;\beta)$$
$$+\frac{\hbar^4}{64}\frac{\beta^2}{M^2}\int_{-\infty}^{\infty} dq\delta''(q)\frac{1}{q^2}\Omega_0(p, q;\beta) = 0. \tag{F21}$$

e. κ_{45}, κ_{46}, and κ_4

As already noted when considering κ_2, for the hexic barrier the first-order-in-$\hbar^2$ contribution to the thermal density goes at least as q^4 and therefore this term also vanishes. For the same reason also κ_{46} vanishes, so that summing it all up we remain with

$$\kappa_4 = 0. \tag{F22}$$

The hexic potential barrier transmission coefficient differs from the classical only for terms going as $\hbar^6$ and higher powers.

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