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Review

A Century of Semiclassics - Tunneling and Quantization

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Abstract: Two quantum effects have had a big impact on Chemistry. Arguably the most important one is the quantization of vib-rotational energy levels, an effect which challenges classical mechanics computations of molecular dynamics and is at the basis of molecular spectroscopy. The second is quantum tunneling which is especially important when considering light atom transfer, especially hydrogen atoms and proton transfer. Tunneling was reported for the first time by Hund in 1927 in his paper which was submitted on Nov. 19, 1926. The quantization of energy levels was one of the major building blocks of the new quantum theory, the semiclassical quantization condition was formulated in the summer of 1927 by Brillouin, Wentzel and Kramers. In retrospect, a century later, we have learned much about the two effects, yet surprisingly, the giants who discovered and formulated the relevant semiclassical theories left us with some challenges. Some of these have been answered during the past five years and these are the main emphasis of this review, which is not a review of 100 years of semiclassics, a project which calls for books, rather than short review articles. At the same time, we point out some remaining challenges which have not been answered, and which demonstrate, that there is always something new to learn even when considering well established theories.

Key words: tunneling, semiclassical, rate theory, quantization.

1. Introduction

One hundred years ago, Brillouin [1], Wentzel [2] and Kramers [3] derived the well known semiclassical quantization rule for energy levels in one dimensional systems

$$S(E_n) = \oint dq\sqrt{2M[E_n - V(q)]} = 2\pi\hbar\left(n+\frac{1}{2}\right). \qquad (1)$$

Here $S(E)$ denotes the action for a system with mass M governed by the Hamiltonian

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

with potential $V(q)$. n is a nonnegative integer. To be more precise, Brillouin and Wentzel's quantization condition was the old Bohr-Sommerfeld quantization rule of $2\pi\hbar n$, the important added factor of $\frac{1}{2}$ was derived by Kramers only. This famous semiclassical result has mostly been referred to as WKB theory, or JWKB theory when adding the earlier (1924) result of Jeffreys [4] obtained in his study of asymptotic expansions. Historically, Kemble [5] in his paper of 1935 refers to the theory correctly as BWK theory, reflecting the historical development. In retrospect, the really new aspect was that of Kramers, and it is this formula which has been used in innumerable contexts during the past century. Henceforth we will refer to the quantization rule of Eq. (1) as Kramers' quantization rule.

The quantization rule has been used extensively to extend the semiclassical result to multi-dimensional systems. The essential idea is that one may approximate the N dimensional Hamiltonian as being classically integrable, so that $H = H(J_1,J_2,\ldots,J_N)$ and each action J_k is quantized as in Kramers' one dimensional result. This is known as Einstein [6], Brillouin [7], Kramers [8] (EBK) quantization. In the EBK method, Kramers' $\frac{1}{2}$ term is replaced by an appropriate Maslov index [9] which in the usual case follows the number of turning points of the relevant underlying orbit. This methodology can be in principle applied on the fly using appropriate Fourier transformation of classical trajectories, as presented for example in Refs. [10,11]. It has also been used in the context of perturbation theory [12].

The second aspect of this subjective review is that of tunneling. A description of the early history was given in a review article by Merzbacher, titled "The Early History of Quantum Tunneling" [13]. Briefly, Hund [14], in a paper submitted on November 19, 1926, discovered tunneling splitting of levels in symmetric molecules. A very short time later, Nordheim [15] solved the transmission and reflection probabilities for scattering on square barriers. Gamow, considered in 1928 α-particle decay of nuclei [16]. He was the first to write down the decay time in terms of the imaginary action integral for motion on the upside down potential barrier. A seminal analytic model was presented in Eckart's 1930 paper [17] where he solved analytically the energy dependent transmission and reflection probabilities through what is now termed as the Eckart barrier. This model potential played an important role in understanding quantum tunneling effects, especially within the Chemistry literature.

A central further development was in Wigner's 1932 paper [18] where he considered the effect of tunneling on thermal chemical reaction rates, deriving the leading $\hbar^2$ tunneling contribution term. His expression showed an increase of the rate as compared to the purely classical result. One of the curious results of this 1932 paper was that Wigner also predicted that quartic nonlinearity of the barrier would increase the rate beyond that which is to be expected from a parabolic barrier approximation. This unexpected increase and its origin was largely ignored until very recently.

From a semiclassical point of view, Kemble's 1935 paper [5] presented almost as an afterthought an essential improvement over Gamow's expression. Using a uniform theory to treat the connection formulae needed to connect the wavefunction in the classically allowed and forbidden regions Kemble derived a uniform expression for the transmission probability

$$T_{usc}(E) = \frac{1}{1+\exp\left(\frac{W(E)}{\hbar}\right)} \tag{3}$$

where the tunneling action for scattering energies below the barrier energy is as in Gamow's theory

$$W(E) = \oint dq\sqrt{2M[V(q)-E]}. \tag{4}$$

For energies above the barrier, one may obtain the action by analytic continuation [19], but a more recent and practical approach is based on quantum perturbation theory, as presented during the years 1990-1993 by Miller, Handy and their coworkers [20–22]. One should note that even at the scattering threshold, the Euclidean action $W(E)$ is finite and the transmission factor, although exponentially small, remains finite. This is incorrect since for sufficiently low energies quantum reflection dominates and the transmission coefficient should tend to 0 [23–25].

Another important milestone in the development of the semiclassical theory was the analytic solution for the transmission and reflection probabilities through a parabolic barrier, as presented by Bell in his 1958 paper [26], though one should add that he already alluded to these results in a comment in his 1935 paper [27] where he explores implications of the semiclassical tunneling formula. He found that for the parabolic barrier potential

$$V_{pb}(q) = V^{\ddagger} - \frac{M\omega^{\ddagger 2}}{2}q^2 \tag{5}$$

the transmission probability is

$$T_{pb}(E) = \frac{1}{1+\exp\left(\frac{2\pi\left(V^{\ddagger}-E\right)}{\hbar\omega^{\ddagger}}\right)}. \tag{6}$$

When averaged over the thermal distribution $\exp(-\beta E)$ $(\beta = 1/(k_B T))$ he obtained an exact expression for the thermal transmission factor

$$\begin{aligned} T_{pb}(\beta) &\equiv \beta\exp\left(\beta V^{\ddagger}\right)\int_{-\infty}^{\infty} d\,E\exp(-\beta E)T_{pb}(E) \\ &= \frac{\hbar\beta\omega^{\ddagger}}{2\sin\left(\frac{\hbar\beta\omega^{\ddagger}}{2}\right)} = 1+\frac{\hbar^2\beta^2\omega^{\ddagger 2}}{24}+O(\hbar^4). \end{aligned} \tag{7}$$

The leading order correction term in $\hbar^2$ is identical to Wigner's parabolic barrier result. It is important to note that when the temperature is lowered to the point at which $\hbar\beta\omega^{\ddagger} = 2\pi$ the parabolic barrier thermal transmission factor diverges. This divergence is due to the fact that as $E \to -\infty$ the transmission probability decreases as $\exp\left(\frac{2\pi E}{\hbar\omega^{\ddagger}}\right)$ while the thermal factor increases as $\exp(-\beta E)$ so that when the temperature becomes too low the contribution from this low energy region dominates and the integral diverges. In practice, there is always a lower limit on the possible incident energy and the divergence is not reached. For the parabolic barrier, Kemble's expression is exact since the Euclidean action is $\frac{2\pi\left(V^{\ddagger}-E\right)}{\omega^{\ddagger}}$. This has been used to approximate the Euclidean action for above barrier scattering [28,29].

Generalization of the semiclassical tunneling formulae to multidimensional systems was first considered by Miller [30] where he discovered what is known today as the instanton - a periodic orbit on the inverted multidimensional potential. By considering a steepest descent approximation and the multidimensional semiclassical approximation to the density as derived by Gutzwiller [31], Miller obtained a semiclassical approximation for the rate. This result has one glaring defect, the pre-factor has in the denominator the second derivative of the action and this second derivative vanishes whenever the steepest descent energy is at the barrier energy. Around the barrier energy, the action is the parabolic barrier action which is linear in the energy so that the second derivative vanishes and the expression diverges. This happens when the temperature is such that $\hbar\beta\omega^{\ddagger}=2\pi$, precisely the temperature at which the parabolic barrier result diverges. At lower temperatures one has the instanton result. At higher temperatures the dominant contribution is the parabolic barrier result. Due to this, the divergence temperature has been termed as the crossover temperature between quantum tunneling and above barrier transmission [32]. In fact, the divergence is not physical, there is no divergence in the exact quantum mechanical energy dependent transmission probability and thermal averaging should not introduce a divergence. Its origin is in the steepest descent approximation used to estimate the thermal energy integral. One would want to have an estimate in which the divergence disappears and one has a smooth prediction valid for all temperatures.

Tunneling is not limited to reactions, Hund's original paper [14] considers the tunneling splitting in a symmetric double well potential. In such cases, one must consider the semiclassics for motion in the well and through the barrier. The one dimensional semiclassical expression for the splitting is [33,34]

$$\Delta E_n = \frac{2\hbar}{\tau(E_n)}\exp\left(-\frac{W(E_n)}{2\hbar}\right) \tag{8}$$

where $\tau(En)$ is the period of motion in the well at the quantized (mean) energy in the well. Of note is the fact that the exponential factor has in it half of the full Euclidean action over one period of the motion on the inverted potential. The semiclassical expression for the tunneling splitting has its roots in a paper by Ford and Wheeler [35]. One notes that the Euclidean action is divided by two, this is peculiar to symmetric systems, in asymmetric systems, as also studied originally by Gamow [16] the full action over one period is the relevant tunneling action. The explanation for this difference was considered in some detail by Miller [34].

A slightly different expression is found when using the imaginary free energy semiclassical theory. The ratio between the two expressions for the ground state splitting is a constant factor of $\sqrt{\frac{e}{\pi}} \simeq 0.93$. The source of the difference is the method of derivation. In the Imaginary Free Energy (ImF) method [36] which underlies the instanton result [37,38], one takes into consideration the fact that the ground state wavefunction is a (harmonic) Gaussian. In the semiclassical theory, one assumes that the wavefunction maximizes in the vicinity of the turning point and this is not true for the ground state but does become a better assumption as one goes up the ladder of energy levels. In any case, from a computational point of view the differences are not very large [39].

We will discuss in Section II some central questions arising from the semiclassical theory, some of which have been addressed only in recent years. Then in Section III we will present recent developments in the semiclassical theory which respond to the questions raised in Section II. We end with a discussion of some of the unanswered challenges, stressing that there probably remain a myriad of additional questions and even some which we still do not even know to formulate.

2. Challenges raised by semiclassics

2.1 Semiclassical quantization

Kramers' expression has been very successful, leading to rather accurate quantization energies, especially in one dimensional oscillator systems. Yet, it has a fundamental flaw [12], it does not agree with second order perturbation theory [40–42]. Specifically, one may separate the potential into a harmonic and anharmonic term

$$V(q) = \frac{M\omega^2}{2}q^2 + \lambda V_1(q) \tag{9}$$

where λ is the perturbation parameter which at the end is set to unity. The anharmonicity may be expanded to fourth order

$$V_1(q) = \frac{V_3}{6}q^3 + \frac{V_4}{24}q^4. \tag{10}$$

Using second order quantum perturbation theory it is well understood that the bound state energies in the well are given by

$$E_n = \Delta E_0 + \hbar\omega\left(n+\frac{1}{2}\right) + X_0\left(n+\frac{1}{2}\right)^2 \tag{11}$$

where the nonlinear parameters are expressed in terms of the second (V_2=$M\omega^2$), third (V_3) and fourth (V_4) derivatives of the full potential at its minimum. The nonlinear coefficient is

$$X_0 = \frac{\hbar^2\omega^2}{16}\left(\frac{V_4}{V_2^2} - \frac{5V_3^2}{3V_2^3}\right) \tag{12}$$

and the constant energy shift is

$$\Delta E_0 = \frac{\hbar^2\omega^2}{64}\left(\frac{V_4}{V_2^2} - \frac{7V_3^2}{9V_2^3}\right). \tag{13}$$

One may similarly expand the classical action integral to find that

$$S(E) \simeq \frac{2\pi}{\omega}\left[E - \frac{E^2}{16}\left(\frac{V_4}{V_2^2} - \frac{5}{3}\frac{V_3^2}{V_2^3}\right) + \ldots\right]. \tag{14}$$

Imposing the quantization condition $S(E) = 2\pi\hbar\left(n+\frac{1}{2}\right)$ and solving the resulting quadratic equation one finds that to order $\hbar^2$ the energy levels are given by the perturbation theory result of Eq. (11) and Eq. (12) but the constant energy factor ΔE_0 is missing [12,43]. It is then natural to ask whether one can modify Kramers' expression such that it would give the precise second order perturbation theory result.

2.2 Thermal tunneling rates

One should distinguish between high and low temperatures. For high temperatures, as noted in the Introduction, Wigner derived the leading order in $\hbar^2$ corrections to the one dimensional thermal barrier crossing rates. However, his derivation was limited to symmetric nonlinear terms, he did not derive the effect of asymmetry, nor did he provide a clue as to how one may derive terms of order $\hbar^4$ and higher. An added challenge coming from his paper is that he finds that the quartic nonlinear term increases the rate as compared to the parabolic barrier result, this even though the nonlinearity broadens the barrier relative to the parabolic barrer so one might expect that it would decrease the rate rather than increase it.

At low temperatures, one typically finds that the various approximations based on instantons give rates that are somewhat lower than the exact results [44]. One may ask why? What is the source of the difference? In this context one should add that as the temperature goes to 0 the rate should vanish due to the quantum reflection phenomenon, clearly then there will be a low temperature at which the instanton based estimates will become too large. It would seem that more insight is needed to understand the ultra-low temperature regime.

There is another difficulty in the semiclassical theory. Kemble's semiclassical expression for the transmission probability is such that when the action vanishes, the probability is precisely $\frac{1}{2}$. This occurs when the incident energy equals the barrier energy irrespective of the details of the shape of the barrier. However, we know that for a square barrier [15] the probability at the barrier energy is less than $\frac{1}{2}$, while for an Eckart barrier [17] it is larger than $\frac{1}{2}$. This "half point" property cannot be ignored [44,45] since the tunneling is exponentially sensitive to the action and therefore the thermal rate would give an incorrect thermal estimate.

A related aspect is that expanding the thermal probability to order $\hbar^2$ as obtained from Kemble's expression leads to the parabolic barrier limit but does not give the correct result as derived by Wigner [44]. The same flaw discussed above for the level quantization shows up in a different way here in terms of the barrier crossing rate.

As discussed above, if one uses the Kemble expression for the energy dependent transmission probability and performs the energy average weighted by the thermal distribution $(\exp(-\beta E))$ there will not be any divergence. The source of the divergence is in the steepest descent evaluation of the integral. A challenge then, which has intrigued many [29,32,39], is whether one can formulate a semiclassical theory for the thermal transmission coefficient without unphysical effects coming from a divergence.

Thus far the discussion has concentrated on one dimensional systems, what happens when going to the real multidimensional world? Instanton theory is not limited to one dimension [30], but the questions discussed above carry over to the multidimensional world as well. There are though aspects which up to date of the writing of this review are limited to one dimension, for example

what is the correct $\hbar^2$ correction term to the classical rate in multidimensional systems?

2.3 Tunneling decay and splitting

As mentioned the semiclassical expression as given in Eq. (8) differs from the ImF result. Originally, the ImF method was used to estimate decay rates in a cubic potential whose form is

$$H = \hbar\omega\left[-\frac{1}{2}\frac{d^2}{dx^2}+\frac{x^2}{2}-2\sqrt{2}\lambda x^3\right]. \quad (15)$$

The barrier height (energy difference between the barrier $x=\frac{1}{6\sqrt{2}\lambda}$ and the well (x=0)) is $V^{\ddagger}=\frac{1}{432\lambda^2}$, it increases inversely quadratically with the magnitude of λ. The instanton result for the ground state decay rate of the cubic potential as defined in Eq. (15) is

$$\Gamma_{0,ins}=\frac{1}{2\lambda\sqrt{2\pi}}\exp\left(-\frac{1}{60\lambda^2}\right) \quad (16)$$

The cubic potential is not symmetric, so that the semiclassical decay rates are

$$\Gamma_{n,sc}=\frac{1}{\tau(E_n)}\exp\left(-\frac{W(E_n)}{\hbar}\right). \quad (17)$$

The resulting lowest resonance energy decay rates are given in **Table 1** in units of ω^{-1} for different values of the cubic coupling parameter λ. The exact rates ($\Gamma_{0,ex}$) are taken from the paper by Yaris et al [46], however they have been recomputed to higher accuracy [43].

The semiclassical estimate as given in Eq. (17) ($\Gamma_{0,sc}$) is substantially more accurate than the instanton result ($\Gamma_{0,ins}$), which does improve as the barrier height increases and the well supports more bound resonance states. In one dimension, the instanton result is a leading order term in a series [47], so that one can get much more accurate instanton based rate estimates. Consistently, the semiclassical result is lower than the exact result while the instanton result is higher. Conversely, it is well understood that the semiclassical result does not take into consideration the ground state wavefunction in the well which maximizes around the well bottom and not the turning point [39]. As one goes up the ladder of states, the semiclassical result is more accurate than the instanton result. On the other hand, the instanton expression is readily generalized to many degrees of freedom [30], doing the same for the semiclassical approximation is not trivial and related to the question of whether the motion in the well is integrable or non-integrable. In other words, although we have semiclassical expressions, they are not fully understood and are much more difficult to generalize to multidimensional systems [48–51].

Table 1. Decay rates for the cubic potential given in Eq. (15).

λ	$\Gamma_{0,ex}$	$\Gamma_{0,sc}$	$\Gamma_{0,ins}$	$\Gamma_{0,msc}$
0.0481	$2.263\cdot10^{-3}$	$2.313\cdot10^{-3}$ (2.2%)	$3.085\cdot10^{-3}$ (36%)	$2.317\cdot10^{-3}$ (2.4%)
0.034	$2.867\cdot10^{-6}$	$2.753\cdot10^{-6}$ (4.1%)	$3.214\cdot10^{-6}$ (12%)	$2.754\cdot10^{-6}$ (4.1%)
0.03	$5.536\cdot10^{-8}$	$5.267\cdot10^{-8}$ (5.1%)	$6.029\cdot10^{-8}$ (8.9%)	$5.268\cdot10^{-8}$ (5.1%)

3. Recent developments

3.1 Semiclassical quantization

In retrospect, it is straightforward to introduce a modification of Kramers' semiclassical quantization condition by shifting the energy:

$$S(E_n-\Delta E_0)=2\pi\hbar\left(n+\frac{1}{2}\right). \quad (18)$$

The constant shift ΔE_0 is just the constant energy shift appearing in second order perturbation theory [43–45]. Since it is of order $\hbar^2$ it is straightforward to show that to lowest order in $\hbar^{2n}$, assuming cubic and quartic nonlinearity as in Eq. (10) one retrieves precisely the second order vibration perturbation theory expression. However, it is important to note that when computing the energy shifted action $S(E-\Delta E_0)$ it contains all orders of the nonlinearity and $\hbar^2$. Our experience is that numerically, this modified quantization condition is superior to the vibrational perturbation theory estimate of the bound state energies. This is demonstrated in **Table 2** for the cubic potential where we provide the numerically exact resonance energies E_n (ex) for the oscillator as given in Eq. (15) and compare them with Kramers' semiclassical estimate E_n (scl) as obtained from Eq. (1), the modified semiclassical estimate E_n (mscl) as given in Eq. (18) and the VPT2 estimate E_n (VPT2), Eq. (11). We note that the standard semiclassical estimate is more or less as accurate as the VPT2 result, but the modified semiclassical result is more accurate than either of the other two.

In **Table 3** we present a similar comparison, but now for the quartic double well potential

$$V(x)=V^{\ddagger}\left(\frac{x^2}{x_0^2}-1\right)^2 \quad (19)$$

and as in the model studied in Ref. [52], we use $x_0=5\sqrt{V^{\ddagger}}$ with unit mass. The VPT2 estimate for the mean doublet energies is

$$E_n=-\frac{1}{400V^{\ddagger}}+\frac{2}{5}\sqrt{2}\left(n+\frac{1}{2}\right)-\frac{3}{100V^{\ddagger}}\left(n+\frac{1}{2}\right)^2. \quad (20)$$

Here, we compare the numerically exact mean doublet energies with the semiclassical Eq. (1), modified semiclassical Eq. (18) and the VPT2 estimate Eq. (20). For the quartic oscillator the Kramers' semiclassical quantization condition is rather accurate, much more than the VPT2 result. Again, however, the modified semiclassical quantization of Eq. (18) is superior to both. The only exception is for the case of $V^{\ddagger}=\frac{1}{4}$ for which the mean doublet energy is very close to the barrier top, where one may expect that the standard semiclassical estimate will not be very good due to the closeness of the orbits in either of the two wells. The critical reader might note that at the end of the day, the semiclassical result without the shift is rather accurate, so is the added correction really important? In this context, one should note that spectroscopic accuracy is of the

order of one or less cm^{-1} so that any improvement in the accuracy of the semiclassical quantization is meaningful.

As discussed in Ref. [43] the modified semiclassical estimate is also exact to order $\hbar^2$ for the Rosen-Morse potential [53], (which is an inverted Eckart barrier) while Kramers' expression is not. In this context we also note that for the Morse potential the zero point energy shift vanishes [54] so that the modified semiclassical quantization is identical to Kramers' semiclassical quantization and it is exact.

Table 2. Resonance energies for the cubic potential given in Eq. (15).

λ	n	E_n (ex)	E_n (scl)	E_n (mscl)	E_n (VPT2)
0.0481	0	0.465164	0.480283 (3.2%)	0.472186 (1.5%)	0.474550 (2.0%)
0.034	0	0.485679	0.490808 (1.1%)	0.486762 (0.22%)	0.487284 (0.33%)
0.034	1	1.391575	1.403338 (0.85%)	1.399292 (0.55%)	1.417924 (1.9%)
0.030	0	0.489195	0.492941 (0.77%)	0.489791 (0.12%)	0.490100 (0.18%)
0.030	1	1.422922	1.429118 (0.44%)	1.425968 (0.21%)	1.436100 (0.93%)
0.03	2	2.250200	2.267590 (0.8%)	2.264440 (0.63%)	2.328100 (3.5%)

3.2 Rate theory

The last few years have seen significant advances in rate theory. Foremost, the challenge emanating from Wigner's paper of 1932, to derive exact general $\hbar^{2n}$ correction terms has been answered for one dimensional systems. The starting point is the exact expression for the transmission coefficient which is defined as the ratio of the exact quantum thermal flux through the barrier to the classical thermal flux [55,56]

$$T(\beta) = 2\pi\hbar\beta \mathrm{Re}\left(\mathrm{Tr}\left[\exp\left(-\beta\widehat{\mathcal{H}}\right)\widehat{F}(\hat{q})\widehat{P}\right]\right) \tag{21}$$

The flux operator, which measures the flux at the barrier top, is defined as

$$\widehat{F}(\hat{q}) = \frac{1}{2M}[\hat{p}\delta(\hat{q}) + \delta(\hat{q})\hat{p}] \tag{22}$$

where $\delta(x)$ denotes the Dirac "delta" function. The projection operator onto the product side is defined as [56]

$$\widehat{P} = \lim_{t\to\infty}\left[\exp\left(\frac{i\widehat{H}t}{\hbar}\right)\theta(\hat{q})\exp\left(-\frac{i\widehat{H}t}{\hbar}\right)\right] \tag{23}$$

and $\theta(\hat{q})$ is the unit step function. It is the projection operator which is difficult to compute, since it demands an infinite time propagation. However the classical projection operator in one dimension is trivial, the momentum must be positive and the incident energy greater than the barrier height of the relevant barrier potential. It is then a matter of some algebra, as delineated in Ref. [57] to find that the leading order expression is

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

This expression was then further extended to order $\hbar^4$ in Ref [58].

Eq. (24) is instructive. First, one notes that the second derivative at the barrier - V_2 is by definition negative so that the asymmetry contribution is always positive. Secondly, typically, the fourth order derivative is positive (as for example in the Eckart barrier) so that the leading order correction gives a transmission coefficient which is greater than the parabolic barrier result. This property is violated when using some of the popular approximation schemes such as centroid [59,60] or ring-polymer molecular dynamics [61,62] and the classical Wigner [63] (also known as the linearization [64–66]) approximation. It is correct though when using the second order vibrational perturbation theory of Refs. [20–22].

The fact that the exact answer is typically larger than the parabolic barrier result is surprising as typically the parabolic barrier is thinner than say an Eckart barrier so the action through the parabolic barrier is expected to be smaller thus leading to a larger transmission coefficient. This puzzle was resolved when considering the half point problem. Second order vibrational perturbation theory implies a quadratic energy Euclidean action relationship [21]

$$E \equiv V^{\ddagger} + \Delta E_0 - \frac{\omega^{\ddagger} W_{VPT2}(E)}{2\pi} - X_0\frac{W_{VPT2}(E)^2}{(2\pi)^2} \tag{25}$$

With

$$\Delta E_0 = -\frac{\hbar^2\omega^{\ddagger 2}}{64}\left(\frac{V_4}{V_2^2} - \frac{7}{9}\frac{V_3^2}{V_2^3}\right) \tag{26}$$

and

$$X_0 = -\frac{\omega^{\ddagger 2}}{16}\left[\frac{V_4}{V_2^2} - \frac{5}{3}\frac{V_3^2}{V_2^3}\right] \tag{27}$$

where $\omega^{\ddagger}$ is the (imaginary) barrier frequency and the derivatives are taken at the barrier. Of special importance is the constant energy component ΔE_0 which is typically negative and implies that the nonlinearity in the barrier leads to an effective lowering of the barrier energy. It is this lowering which implies through Kemble's uniform semiclassical expression, that the action will typically vanish at an energy which is lower than the barrier height $V^{\ddagger}$. The half point then becomes potential dependent, different nonlinear coefficients will lead to different lowerings or sometimes increases in the effective barrier.

By definition, this constant contribution is included in the semiclassical second order vibration perturbation rate theory so that it gives also the correct leading order result for the transmission coefficient [57]. This also explains why the leading order contribution of order $\hbar^2$ is typically larger than the parabolic barrier result - the parabolic barrier does not have higher order derivatives so that ΔE_0 vanishes. The barrier height of the parabolic barrier model is then usually greater than the effective barrier height of the nonlinear barrier and this is responsible for the smaller parabolic barrier transmission coefficient. One may further expand the exact transmission coefficient to order $\hbar^4$ as in Ref. [58] and then one has

an additional contribution to the constant change of the effective barrier height. In practice, this calls for up to the eighth derivative of the potential at the barrier top, not too convenient.

It was well known that the second order vibrational perturbation theory for rates is not accurate for low temperatures [54,67]. This is not surprising, as the low temperature rate is typically determined by the periodic orbit under the barrier which is far away from the barrier top. However, the constant contribution to the barrier height suggested a simple way of correcting the second order theory. Instead of using the Kemble transmission coefficient as in Eq. (3) one shifts it such that [45]

$$T_{mVPT2}(E) = \frac{\theta\left(V^{\ddagger} - E - \Delta E_0\right)}{1+\exp\left(\frac{W(E+\Delta E_0)}{\hbar}\right)} + \frac{\theta\left(E + \Delta E_0 - V^{\ddagger}\right)}{1+\exp\left(\frac{W_{VPT2}(E)}{\hbar}\right)} \quad (28)$$

where $\theta(x)$ is the unit step function, $W(E)$ is the Euclidean action as in Eq. (4) and $W_{VPT2}(E)$ is the Euclidean action as obtained from second order vibrational perturbation theory Eq. (25). This modified second order vibrational perturbation theory expression turns out to be rather accurate when tested on some model systems such as the symmetric and asymmetric Eckart barrier, a Gaussian barrier and the collinear hydrogen exchange reaction [68].

Another interesting aspect of the Kemble modification is that when using the Kemble form to perform the steepest descent estimate of the thermal transmission factor, one solves the divergence problem, there is no divergence at all [69]. This is as it should be since the quantum transmission coefficient is bounded between 0 and 1 and there is no physical reason for a divergence to occur. There is another aspect to this observation. In the "old" literature, the divergence occurs when $\hbar\beta_c\omega^{\ddagger} = 2\pi$ and the (inverse) temperature β_c at which this occurs is referred to as the crossover temperature between tunneling and thermal activation. However, when using the Kemble form for the steepest descent estimate, the temperature at which the incident energy equals the barrier energy is such that $\hbar\beta\omega^{\ddagger} = \pi$. If one defines the crossover temperature as that temperature at which the steepest descent energy equals the barrier height then the crossover temperature is twice as high as the one considered in the "standard" steepest descent estimate. In other words, tunneling is more ubiquitous than previously thought.

Table 3. Mean doublet energies for the quartic potential given in Eq. (19).

$V^{\ddagger}$	n	E_n (ex)	E_n (scl)	E_n (mscl)	E_n (VPT2)
2	0	0.27762	0.27899 (0.49%)	0.27774 (0.04%)	0.27784 (0.08%)
1	0	0.27186	0.27493 (1.13%)	0.27243 (0.21%)	0.27284 (0.36%)
1/2	0	0.25815	0.26594 (3.02%)	0.26094 (1.08%)	0.26284 (1.82%)
1/4	0	0.24773	0.24097 (2.73%)	0.23097 (7.26%)	0.24284 (2.01%)
4	0	0.28029	0.28094 (0.23%)	0.28032 (0.01%)	0.28034 (0.02%)
4	1	0.83025	0.83097 (0.09%)	0.83034 (0.01%)	0.83103 (0.09%)
4	2	1.36317	1.36398 (0.06%)	1.36335 (0.01%)	1.36671 (0.26%)
4	3	1.87726	1.87819 (0.05%)	1.87756 (0.02%)	1.88740 (0.54%)
4	4	2.37013	2.37123 (0.05%)	2.37060 (0.02%)	2.39308 (0.97%)
4	5	2.83837	2.83974 (0.05%)	2.83912 (0.03%)	2.88377 (1.60%)
4	6	3.27657	3.27851 (0.06%)	3.27789 (0.04%)	3.35946 (2.53%)
4	7	3.67408	3.67774 (0.10%)	3.67712 (0.08%)	3.82014 (3.98%)

This modified vibrational perturbation theory as given by Eq. (28) is readily generalized to many dimensions [70], as also evidenced by its successful application to the collinear hydrogen exchange reaction. Indeed, it gives an approximation which is substantially more accurate than a ring polymer molecular dynamics (RPMD) estimate [68]. This is not surprising, as the RPMD method does not include in it the constant energy shift and so is not as accurate both for low temperatures, dominated by tunneling and high temperatures dominated by above barrier energies.

3.3 Tunneling splitting and decay rates

The constant energy shift discussed above is not limited to its use in reactive scattering. It also plays an important role when considering tunneling splitting in the case of a symmetric double well potential or decay rates from metastable states [43,71]. The semiclassical tunneling splitting expression is given in Eq. (8) with the modification of the energy shift both in the pre-factor as given through Eq. (18) and in the exponent as considered in Eq. (28). This modified expression for the tunneling splitting is then

$$\Delta E_{msc} = \frac{2\hbar}{\tau(E_n)}\left[1+\exp\left(\frac{W(E_n-\Delta E_0)}{2\hbar}\right)\right]^{-1} \quad (29)$$

where the mean energy E_n is determined by Eq. (18). As an example we consider the quartic double well potential Eq. (19). The resulting tunneling splittings are given in **Table 4** and **Table 5**. Here, the notations are ΔE_{ex} for the numerically exact tunneling splittings obtained by numerical diagonalization of the Hamiltonian, ΔE_{sc} are the semiclassical estimates obtained from Eq. (8) using Kramers' expression to estimate the doublet mean energies E_n together with Kemble's expression for the tunneling factor and ΔE_{msc} as defined in Eq. (29). In **Table 4** only the ground state tunneling splittings are given, in **Table 5** the excited state doublet splittings are also tabulated for the case $V^{\ddagger} = 4$ where due to the deep well eight doublet states are supported. One notes that the modified semiclassical estimate is superior to the "standard" semiclassical estimate, especially for the lower states.

Similarly, the expression for the decay rate from a metastable state Eq. (17) should be modified to express the constant energy shift. Some numerical results for the cubic oscillator Eq. (15) are given in **Table 1** where $\Gamma_{0,msc}$ denotes the estimate obtained by using the modified Kramers Eq. (18) to derive the energy (given in **Table 2**) and the action is shifted by ΔE_0. One notes that in all cases, the semiclassical based rates are superior to the instanton estimates however, the modified semiclassical rates hardly create a change. The reason for this is that for the cubic oscillator the zero

point energy shift in the well and under the barrier are precisely the same so that the change in energy in the well is compensated by the change in energy under the barrier. For the quartic double well potential this is not the case and the modified theory is the more accurate one.

4. Discussion

We have seen that many of the challenges raised in Section II have been at least partially answered. In one dimension the expansion of the thermal transmission factor has been achieved up to and including the order $\hbar^4$. Yet, the same procedure used for the derivation is not so readily applicable in many dimensions. A critical point is that one needs to know the classical counterparts of the various operators, to implement the expansion. For the thermal operator this has been done already by Wigner in 1932 [72]. The major obstacle is the projection operator. In one dimension the classical projection operator is a simple step function [63]. If the incident energy is above the barrier the particle will cross it, if below, it will be reflected. However, already when going to two dimensions, if the two degrees of freedom are nonlinearly coupled, the classical projection operator is not known analytically. There may be a way to overcome this difficulty by using classical perturbation theory for the classical dynamics, in which the nonlinearity is the "small parameter". This is though not trivial and has yet to be implemented. One may conjecture that the vibrational perturbation theory as derived in many dimensions in Refs. [21,22] does give the correct leading order term in $\hbar^2$ and then use the multidimensional expression for the energy shift. This has been implemented successfully numerically for the collinear hydrogen exchange reaction [68], but a formal derivation is missing. This is not just a mathematical exercise. We have seen that in one dimension practically all other "popular" approximations are incorrect for both low temperatures where tunneling dominates and high temperature where above barrier crossing dominates. We may conjecture that the same occurs in more than one dimension, but the "proof of the pudding" is in derivation of the analytical result.

Table 4. Tunneling splittings for the quartic potential given in Eq. (19).

$V^{\ddagger}$	ΔE_{ex}	ΔE_{sc}	ΔE_{msc}
2	$4.15415\cdot10^{-8}$	$3.89659\cdot10^{-8}$ (6.61%)	$3.92392\cdot10^{-8}$ (5.87%)
1	$3.42299\cdot10^{-4}$	$3.24494\cdot10^{-4}$ (5.49%)	$3.28714\cdot10^{-4}$ (4.13%)
1/2	0.0224867	0.01976839 (13.8%)	0.02022604 (11.18%)
1/4	0.1187560	0.05137751 (231%)	0.05802074 (204.7%)

The constant energy shift derived through vibrational perturbation theory turns out to be critical towards understanding how tunneling affects thermal rates. In second order vibrational perturbation theory it is at least of the order of $\hbar^2$ so that it is perhaps not surprising that this shift has been ignored for almost a century. There are other, perhaps more formal ways of improving semiclassical estimates of rates, as discussed extensively in Refs. [29,73]. However, even these "rigorous" asymptotic derivations have not yet been shown to lead to the correct high temperature correction terms to the rate given in Eq. (24). They hide the "physics". They do not lead to the understanding that quantum mechanics creates an effective lowering or increasing of the barrier height, thus changing the half point for the transmission probability, increasing the rate estimate at low temperatures and leading to high temperature thermal rates that are larger than expected from the parabolic barrier approximation. In this context we also note that the $\hbar^2$ expansion may also indicate systems for which quantum above barrier reflection dominates rather than tunneling [74]. A general understanding of the role of above barrier reflection in chemistry is a challenge for the future.

There is another aspect of quantum reflection which needs to be addressed. It is well known that in the limit of vanishing incident energy, a quantum particle will be reflected - this is known as quantum threshold reflection. None of the semiclassical formulations have this property, so that when the temperature is sufficiently small, all the semiclassical theories considered will overestimate the thermal rate. However, what is the temperature at which the threshold quantum reflection phenomenon kicks in? Can one formulate a "simple" semiclassical theory which also accounts for this challenging quantum phenomenon?

Thus far we have considered only tunneling on a single potential energy surface. It is well understood that tunneling may be observed through the nonadiabatic coupling of two or more electronic states. In the absence of the nonadiabatic coupling the tunneling vanishes. In the presence of coupling the tunneling induced by the nonadiabatic coupling will usually have a smaller probability than the tunneling on the analogous single adiabatic surface [75]. But, is there also an analogous $\hbar^2$ expansion of the thermal tunneling rate? Obtaining analytic results for nonadiabatic thermal tunneling rates is an open problem, yet to be addressed.

Table 5. Tunneling splittings: quartic double well potential $V^{\ddagger} = 4$.

n	ΔE_{ex}	ΔE_{sc}	ΔE_{msc}
0	$3.9126\cdot10^{-16}$	$3.6525\cdot10^{-16}$ (7.12%)	$3.6665\cdot10^{-16}$ (6.71%)
1	$1.5866\cdot10^{-13}$	$1.5508\cdot10^{-13}$ (2.31%)	$1.5558\cdot10^{-13}$ (1.98%)
2	$2.9334\cdot10^{-11}$	$2.8998\cdot10^{-11}$ (1.16%)	$2.9085\cdot10^{-11}$ (0.85%)
3	$3.2524\cdot10^{-9}$	$3.2333\cdot10^{-9}$ (0.59%)	$3.2426\cdot10^{-9}$ (0.30%)
4	$2.3883\cdot10^{-7}$	$2.3839\cdot10^{-7}$ (0.18%)	$2.3905\cdot10^{-7}$ (0.01%)
5	$1.2049\cdot10^{-5}$	$1.2077\cdot10^{-5}$ (0.02%)	$1.2109\cdot10^{-5}$ (0.05%)
6	$4.1486\cdot10^{-4}$	$4.1734\cdot10^{-4}$ (0.06%)	$4.1846\cdot10^{-4}$ (0.09%)
7	$8.9706\cdot10^{-3}$	$8.6034\cdot10^{-3}$ (4.27%)	$8.6257\cdot10^{-3}$ (4.00%)

Much of chemistry occurs in a condensed phase, typically a liquid. Arguably, the simplest possible model for a reaction in a liquid is when the system is coupled bilinearly to a harmonic bath. Such dissipative models abound, the high temperature parabolic barrier model for thermal rates was presented by Wolynes close to fifty years ago [76]. It has been reformulated in terms of transition state theory [77] and expansion of the resulting rate in terms of $\hbar^2$ is well understood [78]. However, the effect of anharmonicity on the rate is not [79]. Application of second order vibrational perturbation theory to such systems is difficult due to the Fermi resonance terms in the second order expressions, which will typically lead to a divergence due to the continuum spectral density of the bath. What is the analog of the change in the barrier energy in such cases? Presumably it is smaller than in the absence of coupling to the bath, but does it disappear altogether? Clearly dissipation and tunneling, although studied extensively in the past [78] leaves us with some fundamental questions which remain unsolved.

We have suggested an extension of Kramers' semiclassical quantization condition, by including in it the constant quantum energy shift Eq. (18). This is readily implemented in one dimension, but what happens if the system has more than one dimension. Kramers' quantization condition has been generalized to integrable systems. In the EBK theory, each independent action is quantized using the condition of Eq. (1). But how does one generalize the shifted condition given in Eq. (18)? How does one identify the constant energy shift associated with each action variable separately? One should formulate a mutlidimensional version of the modified quantization condition which in the least leads upon expansion in the nonlinearity to the result of vibrational perturbation theory, however, this too is an open question.

This review has enumerated some of the challenges facing theory even in the twenty first century. There is no doubt that whether considering quantization or rates, the biggest challenge is to create reliable and accurate methodology which would be applicable to "big" systems, such as proteins, reaction in liquids, etc.. This challenge has been met only partially, however in the context of the present review, it falls outside the scope. A thorough review implies a book, rather than a short article.

In summary, it is remarkable and encouraging, that even a century after the semiclassical work of giants such as Hund, Gamow, Kramers, Wigner and Kemble there is still much to learn about quantum tunneling and quantization. In this review, we have demonstrated that there were some real questions left unanswered, some of which have been clarified only in the past five years. But many challenges remain, some have been delineated here, perhaps others we do not even know, but can only encourage the interested reader, go to it!

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