

Periodic Orbit Approach to the Quantum-Kramers-Rate

Peter Hänggi and Waldemar Hontscha

Lehrstuhl für Theoretische Physik, Universität Augsburg, Memminger Str. 6, D-8900 Augsburg

The quantum analog of Kramers reaction rate for a dissipative environment is derived on the basis of a periodic orbit approach for multidimensional tunneling. The resulting reaction rate expression holds at all temperatures, thus covering [in contrast to the imaginary free energy method (“bounce-”method)] the classical and the quantum regime on the same basis.

Introduction

Quantum reaction rate theory underwent profound developments within the last decade. In particular, the recent progress in the quantum theory in presence of dissipation [1,2,3,4] enables one to generalize the classical theory of Kramers for the rate coefficient in a dissipative environment to the quantum regime [3, 5–9]. Our focus will be on the semiclassical limit of the quantum-transition-state-theory (QTST) in presence of an infinite number of bath degrees of freedom which model the dissipation, i.e. we shall elaborate

on a unified approach to the dissipative quantum Kramers rate in a metastable potential $V(x)$ in which the reaction coordinate x of a reactive particle of mass M is coupled to a continuum of bath degrees of freedom.

Conventional quantum-TST represents a rather patchwork affair: In doing quantum calculations one replaces classical partition functions by their quantum counterparts, assuming separability of the various vibrations and/or rotations near the saddle point, and then corrects for multiple crossings near the barrier top by the multiplication of a temperature-

dependent Wigner-like transmission factor [10,11]. Therefore, this approach essentially restricts the quantum treatment to the high temperature limit. It was only until recently that the case of dissipation (continuum of bath degrees of freedom) has been discussed within this approach in a beautiful paper by Pollak [12].

Within the last decade, the quantum-Kramers rate has originally been studied over the whole temperature regime by the Augsburg-Essen-Polytechnic-Stuttgart school [5, 7, 8, 9, 13, 14] and the Moscow school [6] which all made use of the imaginary-free-energy methodology [15]. The primary object of this latter method is the dissipative bounce (instanton/anti-instanton) solution. This periodic solution – in absence of the influence of dissipation – has been introduced in Miller's semiclassical quantum-TST for non-separable systems [16], see also Refs. [17–20]. Following the original reasoning of Miller [16], we shall re-evaluate the quantum-Kramers rate results [3, 5–9] by use of the multidimensional WKB-approach for the quantum-TST rate in terms of periodic orbit theory [21,22]. In doing so, we cover the whole temperature regime from $T = 0$ up to room temperature on a unified basis. In a previous item [23], see also Refs. [8b,9], we have already reported the results of the continuum limit of this multidimensional WKB quantum rate approach. In this paper, we present a more extended discussion of the various approximations used in arriving at the quantum-Kramer's rate expressions, and give additional new results.

Quantum Reaction Rate Theory

Throughout the following we shall assume that there exists a true time-scale separation for the dynamics within the locally stable state at $x = x_0$, i.e. $V(x_0) = 0$, and the dynamics characterizing the passage through the bottleneck of the metastable potential, $V(x)$ (e.g. a cubic potential) separating products from reactants. Then, an initial nonequilibrium population decays exponentially for times longer than the typical time-scale for nonactivated molecular processes within the well. Thus, the rate coefficient k becomes truly time-independent; it can formally be expressed as the flux integral [24,25]

$$k = Z_0^{-1} \text{Re}[\text{Tr}\{\exp(-\beta H) \delta(x) (p/M) \mathcal{P}\}]. \quad (1)$$

Here, Tr denotes the trace, β denotes the inverse temperature and Z_0 is the partition function of the metastable state at $x_0 < 0$, $x = 0$ indicates the transition state, and \mathcal{P} is the operator that projects onto positive momentum states p in the infinite future ($t \rightarrow \infty$). H denotes the total (system plus bath) Hamiltonian operator. The reaction coordinate x of the escaping particle ranges from $x = -\infty$ to $x = +\infty$. With a few manipulations this formally exact rate expression can be cast as an integral over a flux-flux autocorrelation $C(t)$, i.e. [26]

$$k = Z_0^{-1} \int_0^{\infty} C(t) dt \quad (2)$$

where with $t_c = t - i\hbar\beta/2$

$$C(t) = \text{Tr} [\hat{F} \exp(iH t_c^*/\hbar) \hat{F} \exp(-iH t_c/\hbar)], \quad (3)$$

wherein $\hat{F} = \frac{1}{2} [\delta(x) (p/M) + (p/M) \delta(x)]$ is the symmetrized flux operator.

Semiclassical Quantum-Transition-State-Theory

Following Miller [16] the quantum – TST approximation to the rate k consists in the replacement in (1):

$$\delta(x) (p/M) \mathcal{P} \rightarrow \frac{1}{2} \delta(x) |\dot{x}|, \quad (4)$$

and then proceeds by use of the *semiclassical* approximation for the Boltzmann propagator. Thus, one obtains [16]

$$k \rightarrow k_{\text{TST}} = Z_0^{-1} \text{Re} \left\{ \int dq \langle q | \exp(-\beta H) | q \rangle \delta(x) \frac{1}{2} |\dot{x}| \right\}. \quad (5)$$

Here, $q \equiv (q_0 = x, q_1, \dots, q_N)$ are the coordinates of all the degrees of freedom of the system, (x) and bath, (q_1, \dots, q_N). In going from (1) to (5) we made use of a Weyl ordering for the operator $\delta(x) |\dot{x}|$, [16], i.e. we can replace the trace in (1) by the phase-space average over the Wigner function. By use of the semiclassical expression for the propagator $\exp(-\beta H)$ the corresponding phase space [16] integration has – in consistency with the use of the semiclassical result – been evaluated within the stationary phase approximation (SPA). This procedure then yields (5). Continuing in this vein and evaluating the trace in (5) also in SPA yields a continuum of stationary phase points. This continuum of SPA-points just defines the unstable periodic orbit, or the bounce solution [16]. In view of the Boltzmann propagator, however, this periodic orbit exists for pure negative imaginary times only, i.e. the Wick rotated time $t \rightarrow \tau = it$, is real and positive. We now measure distance along this periodic orbit, $q_0 \equiv x$, with all other coordinates being orthogonal displacements away from it. Therefore, all the integrations over the orthogonal displacements can again be evaluated within SPA. In terms of the Green's function

$$\begin{aligned} \frac{1}{E + i\epsilon - H} &= \frac{-i}{\hbar} \int_0^{\infty} dt \exp \left\{ \frac{i}{\hbar} (E + i\epsilon - H) t \right\} \\ &\equiv G(E + i\epsilon) \end{aligned} \quad (6)$$

we have with

$$\exp(-iHt/\hbar) = \frac{i}{2\pi} \int dE \exp(-iEt/\hbar) G(E), \quad (7a)$$

and $\beta = it/\hbar$ the formal identity

$$\exp(-\beta H) = \lim_{\epsilon \rightarrow 0^+} \frac{i}{2\pi} \int_{-\infty}^{\infty} dE \exp(-\beta E) G(E + i0^+). \quad (7b)$$

Inserting (7) into (5) yields the rate coefficient k_{TST} as a *Boltzmann average*

$$k_{\text{TST}} = Z_0^{-1} \text{Re} \left\{ \frac{i}{2\pi} \int_0^\infty dE \exp(-\beta E) \cdot \int dq \delta(q_0) \frac{1}{2} |\dot{q}_0| \langle q | G(E + i0^+) | q \rangle \right\}. \quad (8)$$

In virtue of this expression involving the Green's function one never has to construct a multidimensional wave function. This feature represents a great advantage when treating the effects of dissipation.

The trace in (8) can now be evaluated by use of unstable periodic orbit theory [22]. Integrating within SPA over the orthogonal fluctuations, with $q = q_0$ fixed, and then integrating over q_0 (which is trivially accomplished due to the δ -function in (8)) yields Miller's central result [16]

$$k_{\text{TST}} = Z_0^{-1} \frac{1}{2\pi\hbar} \int_0^\infty dE \exp(-\beta E) k(E), \quad (9a)$$

where the cumulative reaction probability reads

$$k(E) = \sum_{n=1}^{\infty} (-1)^{n-1} \exp[-n\phi(E)/\hbar] \cdot \prod_{i=1}^N \left\{ 2 \sinh \left[\frac{1}{2} n T(E) \omega_i(E) \right] \right\}^{-1}. \quad (9b)$$

Here, $\phi(E)$ is the abbreviated (Euclidean) action integral along the unstable periodic orbit of period $T(E) = -\phi'(E)$ on the inverted potential landscape (Wick rotation of time $t = -iT(E)$). The set $\{\omega_i(E), i = 1, \dots, N\}$ are the stability (angular) frequencies of the unstable periodic orbit. If, $\phi(E)$ is positive (low temperatures) we note that only the $n = 1$ term contributes significantly to (9a).

Next we use the selfconsistent solution of

$$E_T = E - \sum_{i=1}^N \left(n_i + \frac{1}{2} \right) \hbar \omega_i(E_T) \quad (10)$$

as the energy E_T which is left in the reaction coordinate while the system is crossing the saddle point with the bath being excited $\{n_i\}$ in corresponding modes. Following the reasoning of Miller [27] which he put forward to obtain the improved quantum condition for the eigenvalues of an ergodic system, we now construct an improved, and rather appealing expression for $k(E)$, i.e. following Hänggi and Hontscha [23] we use the tunneling energy in (10) and set [9, 23]

$$k(E) = \sum_{(n_1, \dots, n_N)=0}^{\infty} \left\{ 1 + \exp[\phi(E_T)/\hbar] \right\}^{-1}. \quad (11)$$

In doing so, we have "unexpanded" the corresponding expression in (9b) which results if the sinh-fcts are expanded into geometric series (for more details, see Refs. 9, 28).

Eq. (11) represents a uniform WKB-approximation to $k(E)$, which becomes exact in multidimensional, separable parabolic-like potential landscapes. We stress that (11) accounts for the anharmonic nonlinearities in the reaction coordinate x ; but neglects the influence of anharmonicities for the "transverse" bath degrees of freedom.

With $k(E)$ given in (11), the quantum-TST rate is obtained by insertion of (11) into (9a) and then performing the remaining summations and the integration over the range of total energy E of system plus bath. It also should be noticed that this procedure yields a closed expression for the multidimensional quantum TST-rate that holds true for all temperature [23]. Further, with the density of states for a harmonic oscillator, i.e. $\rho(E) = (2\pi\hbar/T(E))^{-1}$ it follows on inspection of (9a) that the quantity

$$\Gamma(E) = k(E)/T(E) \quad (12)$$

denotes a *semiclassical expression for the microcanonical rate coefficient at total conserved energy E*.

Periodic Orbits: A Useful Identity

Before we proceed to evaluate more explicitly the dissipative quantum-Kramers rate in the continuum limit we shall reconcile the various approximations leading to (9). First the trace operation in (5) naturally leads within the semiclassical limit to the consideration of periodic orbits which give the dominant contributions to (5). In view of the Boltzmann propagator $\exp(-\beta H)$, such periodic orbits, which pass through the transition state location (see (8)), *do not exist in real time* but only in (negative) imaginary time $t = -i\tau$, i.e. $\tau = it$. Therefore, it is advantageous to consider the Euclidean version of the propagator. In original time t , such negative imaginary time periods imply for the SPA-evaluation of (6) a distortion of the integration path into the lower complex half-plane. In other words, we analytically continue the semiclassical propagator $\langle q | \exp(-iH t/\hbar) | q \rangle$ to complex times $t = -i\tau$. The analytically continued Green's function then formally reads [28]

$$\langle q | G(E) | q \rangle \rightarrow \langle q | G_c(E) | q \rangle \equiv \frac{-1}{\hbar} \cdot \int_0^\infty d\tau \exp(E\tau/\hbar) \langle q | \exp(-\tau H/\hbar) | q \rangle. \quad (13)$$

The time integration inherent in (13) must be understood to be performed in SPA with the integration path deformed so as to go through the stationary points in the direction of steepest descent. This procedure is consistent with the use of the semiclassical approximation. Such an approach generally requires some care near conjugate points [focal surfaces], see [29]. This SPA integration fixes the period of the periodic orbit $\tau_{\text{period}} = T(E)$, such that the corresponding classical energy of the periodic orbit equals the value $E = E_{\text{periodic orbit}}$. The final trace over q in (8) is then calculated following the recipe of Gutzwiller [22]; i.e. all the transverse displacements along the periodic orbit are again evaluated

in SPA, while the final integration over q_0 would simply yield the period $T(E)$. By accounting for multiple transversals of the periodic orbit, $T(E) \rightarrow n T(E)$, and keeping track of the phase changes of the periodic orbit at conjugate points yielding the phase $(-1) \cdot (-1)^{n-1}$, one obtains for the trace of the analytically continued Green's function $G_e(E + i0^+)$ $\equiv \frac{-1}{\hbar} \int_0^\infty d\tau \exp(\tau E/\hbar) \exp(-\tau H/\hbar)$ by use of the Refs. [16, 22] the result [28]

$$\int dq \langle q | G_e(E + i0^+) | q \rangle = \frac{(-i)}{\hbar} [i T(E)] \cdot \sum_{n=1}^{\infty} (-1)^{n-1} \exp(-n\phi(E)/\hbar) \cdot \prod_{i=1}^N \left\{ 2 \sinh \left[\frac{1}{2} n T(E) \omega_i(E) \right] \right\}^{-1}. \quad (14)$$

Note that in (13) the fundamental period $T(E)$ is obtained independent of the number of periods. This is so because $T(E)$ stems from an integration over q_0 , and not over time τ . The multiple traversals must be accounted for because to obtain the SPA result we must sum over all solutions for the period $T(E) \equiv T_e(E)$ yielding a fixed energy E [30, 31]. Thus, we deal with an infinite sequence of stationary points along the (negative) – imaginary time axis, $t_n = -inT(E)$; i.e. $\tau_n = nT(E)$. More generally, the result in (13) would be improved further along the line of reasoning of Hänggi, Weiss and Riseborough [32] by including not only real times τ , but also complex-valued time periods $\tau_{nk} \dots = nT_e(E) + ik T_m(E) + \dots$, yielding a fixed energy E . Here, the index e stands for “Euclidean” and m for “Minkowskian”, in reference to the corresponding regions of the non-inverted, original potential landscape such as the barrier region (e), or the reactant and/or product region (m). In particular, *apart* from the normalization factor Z_0^{-1} the rate expression in (9a) is observed to include information about the classically forbidden region (transition-state region) only. Thus, just as with the imaginary free energy bounce formalism – any interference effects to the decay rate stemming from the classically allowed quantum dynamics in the non-inverted potential landscape is not accounted for. Such effects, for example, include backscattering from reactant regions [32], and/or curvature effects of the classically allowed reaction paths.

In Gutzwiller's procedure, the trace is calculated keeping the fluctuations zero at a fixed point on the periodic orbit, and integrating over these fixed points at the end (yielding the period $T(E)$). Likewise, the trace can be evaluated by considering all closed orbits and allowing both for longitudinal and transversal fluctuations around a fixed periodic orbit $\bar{q}(\tau)$. For the trace of the Wick-rotated Green's function

$$\int dq \langle q | G_e(E) | q \rangle = \frac{-1}{\hbar} \int_0^\infty d\tau \exp(\tau E/\hbar) \text{Tr}[\exp(-\tau H/\hbar)] \quad (15)$$

one alternatively can evaluate the semiclassical limit following the reasoning of Callan and Coleman [20]. Use of the SPA (in function space) for the trace in (15) yields stationary solutions obeying $\bar{q}(0) = \bar{q}(\tau)$. Among those are two constant solutions $\bar{q}(\tau) = x_0$ characterizing the stable state dynamics (i.e. it yields Z_0 , see below), and $\bar{q}(\tau) = 0$, characterizing the barrier motion. In view of (8) we consider now only periodic paths passing forth and back the transition state. We shall restrict the following discussion to low temperatures; i.e. the rate controlling relevant energies E in the expression (9a) all are lying below the barrier energy $E = E_b$. With this in mind, we consider for (15) such τ -values for which the nontrivial periodic solution $\bar{q}(0) = \bar{q}(\tau)$ is real-valued. Setting for a general periodic path

$$q(\tau') = \bar{q}(\tau') + \sum_n c_n x_n(\tau'), \quad (16)$$

with $x_n(\tau')$ obeying periodic boundary conditions $x_n(0) = x_n(\tau)$, one considers – for small \hbar – terms in the action up to quadratic order only. In our case, we consider the Euclidean Lagrangian for a harmonic bath coupled bilinearly to the nonlinear reaction coordinate x .

$$L_e = \frac{M}{2} \dot{x}^2 + V(x) + \sum_{i=1}^N \frac{1}{2} m_i \left\{ \dot{q}_i^2 + \left(\Omega_i q_i + \frac{C_i}{m_i \Omega_i} x \right)^2 \right\}. \quad (17)$$

Following the standard procedure, one finds after integrating first over the harmonic bath degrees of freedom in terms of the dissipative bounce trajectory $\bar{q}(\tau)$ and the well-known non-local (Euclidean) Lagrangian L_{eff} [5–9, 13, 14] for the trace the result [28]

$$\text{Tr}[\exp(-\tau H/\hbar)] = iA \tau \left(\frac{S_0}{2\pi\hbar} \right)^{1/2} \prod_{i=1}^N \left[2 \sinh \left(\frac{1}{2} \tau \Omega_i \right) \right]^{-1} \cdot |\det' \delta^2 S_e|_{\bar{q}}^{-1/2} \exp[-S_e(\bar{q}, \tau)/\hbar], \quad (18a)$$

where

$$S_0 = M \int_{-\tau/2}^{\tau/2} du (\dot{\bar{q}}(u))^2, S_e = \int_0^\tau L_e(\bar{q}, \dot{\bar{q}}) du = \int_0^\tau L_{\text{eff}}[\bar{q}, \dot{\bar{q}}] du. \quad (18b)$$

\det' indicates that the Goldstone mode contribution of the eigenvalue zero must be omitted. A is a normalization constant to be determined below. The τ -integration in (15) is again calculated in SPA. This yields the condition $E = \partial S_e / \partial \tau$, i.e. this fixes the period $\tau_{\text{SPA}} \equiv T(E)_{\text{SPA}}$ to equal the total energy E , i.e. $S_e = \phi(\bar{q}) + T(E)E$. With E in the classically forbidden regime we need to consider the primitive orbit only of period $T(E)$, i.e. $G_e \cong G_e^{(1)}$. Insertion of (18) into (15) yields

$$\int dq \langle q | G_e^{(1)}(E + i0^+) | q \rangle = \frac{A}{\hbar} S_0^{1/2} T(E) \cdot [\det' \delta^2 S_e|_{\bar{q}} (-\partial^2 S_e / \partial \tau^2)_{T(E)}]^{-1/2} \cdot \left\{ \prod_{i=1}^N \left[2 \sinh \left(\frac{1}{2} T(E) \Omega_i \right) \right]^{-1} \right\} \exp[-\phi(E)/\hbar]. \quad (19)$$

Hereby we observe that the SPA yields a phase $i = \exp(i\pi/2)$, which with $(-1) iA(i) = A$ yields a real quantity for the analytically continued object (14, 15). The normalization constant, A , stemming from the measure over $\{c_n\}$, can be obtained if we evaluate Z_o , i.e. we use $\bar{q}(0) = \bar{q}(\tau = T(E)) x_o$. This yields [28]

$$Z_o = A |\det \delta^2 S_e|_{\bar{q}=x_o}^{-1/2} \prod_{i=1}^N \left[2 \sinh \left(\frac{1}{2} T(E) \Omega_i \right) \right]^{-1} \quad (20a)$$

$$= \prod_{i=0}^N \left[2 \sinh \left(\frac{1}{2} T(E) \lambda_i^o \right) \right]^{-1}. \quad (20b)$$

Here, the set $\{\lambda_i^o\}$, $i = 0, 1, 2, \dots, N$, are the normal mode (angular) frequencies at the metastable state $\bar{q} = x_o$. Upon expressing A by use of (20b), one finds with n set equal to one upon the comparison of (19) with (14) the important identity:

$$S_o^{1/2} \left(\frac{|\det \delta^2 S_e|_{\bar{q}=x_o}}{|\det \delta^2 S_e|_{\bar{q}(\tau)}} \right)^{1/2} = Z_o^{-1} \left(-\frac{\partial^2 S_e}{\partial \tau^2} \right)_{\tau=T(E)}^{1/2} \cdot \prod_{i=1}^N \left[2 \sinh \left(\frac{1}{2} T(E) \omega_i(E) \right) \right]^{-1}. \quad (21)$$

This relation is of use for the explicit evaluation of determinants. Note also, that in contrast to (14), the SPA in the time integration for (19) is performed here at the end, while for (14) it defines the first step in the approximation scheme, thereby fixing the period $\tau = T(E)$.

The Quantum Kramers Rate

Following Hänggi and Hontscha [23], we now present explicit results for the Kramers rate of a particle that interacts with a continuum ($N \rightarrow \infty$) of bath modes, cf. (17). In terms of the spectral function

$$J(\omega) = \frac{\pi}{2M} \sum_{i=1}^{\infty} \frac{C_i^2}{m_i \Omega_i} \delta(\omega - \Omega_i), \quad (22)$$

the Laplace transform the memory-friction kernel $\gamma(t)$ can be expressed as

$$\hat{\gamma}(z) = \frac{2}{\pi} \int_0^{\infty} d\omega \frac{J(\omega)z}{\omega(z^2 + \omega^2)}. \quad (23)$$

First, we shall consider high temperatures T above the cross-over temperature T_o [5], i.e. with k_B the Boltzmann constant

$$T > T_o = \frac{\hbar}{2\pi k_B} \mu \quad (24)$$

where μ denotes the positive root of

$$\mu = \left[\frac{\hat{\gamma}^2(\mu)}{4} + \omega_b^2 \right]^{1/2} - \frac{1}{2} \hat{\gamma}(\mu) \quad (25)$$

and $\omega_b = |M^{-1} V''(q_o = 0)|^{1/2}$. In other words, μ denotes the dissipation-modified normal mode barrier frequency $\omega_b \rightarrow \mu(\hat{\gamma})$. With $E_T > E_b$, the effective abbreviated action $\phi(\bar{q})$ is negative. Thus the cumulative reaction probability is not exponentially sensitive, and with $k_B T/E_b \ll 1$, anharmonic corrections are negligible. Thus we can use a harmonic approximation, i.e. the period $T(E)$ assumes a constant value $T(E) = 2\pi/\mu$ and the stability frequencies can be approximated by the normal modes in the saddle point region, i.e. $\omega_i(E) \rightarrow \lambda_i^b$. The abbreviated action thus reads

$$\phi(E_T) = (E_b - E_T) 2\pi/\mu < 0. \quad (26)$$

Upon an interchange of the integration in (9a) with the summations we find

$$k_{\text{TST}} = Z_o^{-1} \frac{1}{2\pi\hbar} \sum_{n_1, \dots, n_N=0}^{\infty} \exp \left\{ -\beta [E_b + \sum_i \left(n_i + \frac{1}{2} \right) \hbar \lambda_i^b] \right\} \int_0^{\infty} dE \frac{\exp \left\{ \beta [E_b + \sum_i \left(n_i + \frac{1}{2} \right) \hbar \lambda_i^b - E] \right\}}{1 + \exp \left\{ \beta_o [E_b + \sum_i \left(n_i + \frac{1}{2} \right) \hbar \lambda_i^b - E] \right\}}, \quad (27)$$

where $\beta_o \equiv 2\pi(\hbar\mu)^{-1}$. Setting

$$x = \exp \left\{ \beta [E_b + \sum_i \left(n_i + \frac{1}{2} \right) \hbar \lambda_i^b - E] \right\},$$

the integral in (27) becomes with $x_o = x(E \equiv 0)$

$$\beta^{-1} \int_0^{x_o} dx \frac{1}{1 + x^{\beta_o/\beta}} = \beta^{-1} \left[\int_0^{\infty} \frac{dx}{1 + x^{\beta_o/\beta}} - \int_{x_o}^{\infty} \frac{dx}{1 + x^{\beta_o/\beta}} \right] = \frac{\pi}{\beta_o} [\sin(\pi\beta/\beta_o)]^{-1} - \frac{x_o^{-(\beta_o - \beta)/\beta}}{(\beta_o - \beta)} \varepsilon, \quad (28)$$

where $\frac{1}{2} < \varepsilon < 1$. With $\beta E_b \gg 1$, this correction can be neglected to give after corresponding summations

$$k_{\text{TST}} = \frac{\mu}{2\pi} \frac{2 \sinh(\hbar\beta\lambda_o^o/2)}{2 \sin(\hbar\beta\mu/2)} \left\{ \prod_{i=1}^N \frac{2 \sinh(\hbar\beta\lambda_i^o/2)}{2 \sinh(\hbar\beta\lambda_i^b/2)} \right\} \exp(-\beta E_b), \quad (29)$$

By use of the Pollak identities [12], the products in (29) can be related directly to the dissipation $\hat{\gamma}$, i.e.

$$k_{\text{TST}}(T > T_o) = \left(\frac{\mu\omega_o}{\omega_b 2\pi} \right) \exp(-\beta E_b) \cdot \prod_{n=1}^{\infty} \frac{\omega_o^2 + n^2 v^2 + n v \hat{\gamma}(nv)}{-\omega_b^2 + n^2 v^2 + n v \hat{\gamma}(nv)} \quad (30)$$

where $v = 2\pi/\hbar\beta$, $\omega_o^2 = M^{-1} V''(x = x_{\text{well}})$.

At temperatures $T \cong T_0$, the above approximation diverges at $T = T_0$ proportional to $(T - T_0)^{-1}$. Thus, near $T \cong T_0$ we must account for the nonlinearities of the potential landscape. Setting more accurately [23]

$$\phi(E_T) = (E_b - E_T) \frac{2\pi}{\mu} + \frac{1}{2} (E_b - E_T)^2 |T'(E_b)|, \quad (31)$$

and proceeding as above we arrive at

$$k_{\text{TST}}(T \sim T_0) = \frac{\omega_0}{\omega_b} \frac{\sin(\hbar\beta\mu/2)}{(2\pi\hbar|T'|)^{1/2}} \cdot \prod_{n=1}^{\infty} \frac{\omega_0^2 + n^2 v^2 + n v \hat{\gamma}(nv)}{-\omega_b^2 + n^2 v^2 + n v \hat{\gamma}(nv)} \cdot \exp\left[-\beta E_b + \frac{\hbar(\beta_0 - \beta)^2}{2|T'|}\right] \text{Erfc}\left[\left(\frac{\hbar}{2|T'|}\right)^{1/2} (\beta - \beta_0)\right] + O[\exp(-\beta_0 E_b)/(\beta_0 E_b)^{1/2}], \quad (32)$$

where $\text{Erfc}(x) = 2\pi^{-1/2} \int_{-\infty}^x dy \exp(-y^2) = \text{erfc}(-x)$. With $v^2 - \omega_b^2 + v\hat{\gamma}(v) \equiv a(T - T_0)/T$ we recover the known result of the imaginary free energy method [6, 7, 8, 9, 14, 23, 33].

At low temperatures $T < T_0$, the cumulative reaction probability becomes with $\phi(E_T) > 0$ exponentially small and we must treat the full nonlinearity of the potential. The integration in (9a) can then be approximated by keeping only the term with $n = 1$.

This integration can be performed within SPA to yield [8b, 9]

$$k_{\text{TST}}(T < T_0) = Z_0^{-1} (2\pi\hbar|T'(E_\beta)|)^{-1/2} \exp(-S_b/\hbar) \cdot \prod_{i=1}^N \left[2 \sinh\left(\frac{1}{2} \hbar \beta \omega_i(E_\beta)\right)\right]^{-1} \quad (33)$$

where $T' = \partial T/\partial E$. The SPA condition yields $T(E) = \hbar\beta$, and $E_\beta \equiv E[T(E) = \hbar\beta]$ denotes the corresponding stationary phase energy. S_b is the dissipative bounce action of the periodic orbit with period $\hbar\beta$, i.e.

$$S_b = \int_0^{\hbar\beta} L_{\text{eff}}(\tau) d\tau. \quad (34)$$

Upon noticing that

$$\left(\frac{-\partial^2 S_c}{\partial \tau^2}\right)_{\tau=\hbar\beta}^{-1} = \frac{\partial^2 \phi(E)}{\partial E^2} \Big|_{E=E_\beta} = |T'(E_\beta)| > 0 \quad (35)$$

we find by use of the identity in (21) the alternative expression, i.e.

$$k_{\text{TST}}(T < T_0) = \left(\frac{S_0}{2\pi\hbar}\right)^{1/2} \left(\frac{\det \delta^2 S_c|_{\bar{q}=x_0}}{|\det' \delta^2 S_c|_{\bar{q}(0)=\bar{q}(\hbar\beta)}}\right)^{1/2} \exp(-S_b/\hbar). \quad (36)$$

This latter form precisely equals the imaginary free energy result [3, 5–9, 14].

Conclusions

By use of the semiclassical TST of Miller [24] and the periodic orbit theory we managed to obtain from (9a, 9b, 11) all the previously derived results for the quantum-Kramers rate. This approach has for all temperatures the same common basis, i.e. the rate expression in (9a). We have thus demonstrated that the continuum limit of this quantum TST precisely equals the dissipative quantum-Kramers theory. At high temperatures $T \gg T_0$, the results approach up to quantum corrections (see Ref. [34]), the classical Kramers rate derived fifty years ago [9, 35], i.e.

$$k_{\text{TST}}(T \gg T_0, N \rightarrow \infty) \rightarrow k_{\text{Kramers}} = \frac{\mu}{\omega_b} \frac{\omega_0}{2\pi} \exp(-\beta E_b), \quad (37)$$

where for zero memory friction [35], $\gamma(t) \rightarrow 2\gamma \delta(t)$, i.e. $\hat{\gamma}(\mu) = \gamma$

$$\mu = \left(\frac{\gamma^2}{4} + \omega_b^2\right)^{1/2} - \frac{1}{2}\gamma. \quad (38)$$

The above given results therefore generalize the classical treatment of Kramer's dissipative rate to the full (dissipative) quantum regime which extends from $T = 0$ up to room temperatures.

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