Variational theory of activated rate processes for an arbitrary barrier

Alexander N. Drozdov*
Department of Chemistry, University of California, Davis, California 95616
(Received 10 February 2000)

The thermally activated escape of a Brownian particle over a smooth barrier of arbitrary shape and height is considered as an eigenproblem of the Fokker–Planck equation. For the case of moderate and large friction, the least nonzero eigenvalue of this equation is found via a Rayleigh-quotient-based perturbation method. A comparison with existing variational approaches and from numerical simulations for bistable potentials with parabolic and quartic barriers shows that the proposed expression gives unprecedentedly accurate results at all barrier heights including the limit of vanishingly low barrier.

PACS number(s): 05.40.−a, 82.20.Db, 82.20.Fd

I. INTRODUCTION

The phenomenon of thermally activated escape of a classical system over a potential barrier arises in a multitude of scientific contexts, but the main motivation to study it stems from its connection to chemical reactions [1–4]. Since the fundamental contribution of Kramers [1], much work in this field has been devoted to a simple stochastic model. The model consists of a single mechanical particle moving on a bistable potential $U(x)$, such that it may switch from one metastable ($x<0$) state to another ($x>0$) by crossing over a potential barrier at $x=0$ of height E. The energy necessary to cross the barrier is supplied by the surrounding heat bath, which causes a velocity proportional friction force and a random force. The rate Γ at which the system approaches equilibrium is given by the least nonvanishing eigenvalue λ_1 of the corresponding Fokker–Planck operator (2.2), $\Gamma=\lambda_1$ [9]. Kramers showed that for low friction this rate is limited by the slow diffusion of energy to the particle from the the bath and so is proportional to the friction. In the present paper we will only consider the case of moderate and large friction (also known as the spatial diffusion regime), when the process is limited by the spatial rate of diffusion of the particle across the barrier.

A wide variety of different methods have been used during the past 2 decades to solve Kramers' problem. (For the history of their development up until a decade ago, see the book by Risken [5] as well as Ref. [6]. The present state of the art may be found in Refs. [7] and [8].) Despite the great diversity of these methods, one could broadly subdivide them into two general approaches. One is to recognize the difficulty of obtaining exact analytical expressions excepting some special cases, such as a purely parabolic barrier, and proceed to find the exact result computed numerically. A number of efficient methods for numerically integrating Brownian motion on a grid have been devised, such as finite-difference schemes [10], basis set expansions [5,11–13], trajectory simulation methods [14], and path integral techniques [15,16]. An obvious advantage of this approach is its universal applicability. The afore-mentioned methods can, in principle, provide very accurate results for the rate in a potential with an arbitrarily shaped barrier of any height. However, the required computational effort may be substantial, as the numerical methods suffer from various different shortcomings. In particular, the utility of basis set expansions and finite-difference schemes is strongly limited by the storage requirements and execution time that both grow exponentially with the number of coupled degrees of freedom. For a finite-difference representation, the requirement of numerical stability severely restricts the permitted time step. This is also true for trajectory simulation methods, which are less restrictive with respect to the dimensionality than the above mentioned schemes. A disadvantage of these methods is that they suffer from statistical errors. Usually, one has to generate a huge number of trajectories to reach an accuracy of 1%. The path integral formulation of the Fokker–Planck equation provides a numerically stable solution, which is free of statistical errors and requires a computational effort that increases only slowly with the dimensionality of the system. Its efficacy, however, depends crucially on the accuracy of the short time propagator used.

A second approach was to replace rigor with reasonable approximations. The enormous theoretical literature has evolved Kramers' theory in many directions that include generalizations to systems with many degrees of freedom [17], cases without detailed balance [4,18–21], and non-Markovian dissipation models [22–25], extensions to the full damping range [24–31], improvements of the Kramers method in the weak [24–28,30–33] and moderate-to-strong [5,12,20,25,26,29–31,34–48] friction regimes. The apparent advantage of having analytical formulas for the rate as compared to numerical results of numerical methods is in the simplicity of analyzing such formulas with respect to the variation of parameters. It is often the case that having an analytical formula gives more information about the system studied than just numbers. On the other hand, it is clear that approximate methods could be accurate only if the specific assumptions on which they are based are satisfied. Thus for instance, most of the existing rate theories are strongly dependent on a *parabolic* approximation for the barrier. However, this assumption is not always met in experimental situations. Another common disadvantage is that the barrier height E is assumed to be much larger than the energy of thermal motion $\beta E \gg 1$. Of course, the presence of a rela-

*Permanent address: Institute for High Temperatures, 13/19 Izhorskaya Street, 127412 Moscow, Russia.

tively high barrier is vital for the notion of metastability. For this purpose, however, a barrier of already order k_BT will suffice to separate the interwell equilibration time $\tau_f e^{\beta E}$ from the fast time scale τ_f on which the intrawell relaxation takes place. In the above-mentioned asymptotic theories $(\beta E)^{-1}$ itself, rather than $e^{-\beta E}$, enters as a small parameter; accordingly, the theories do not cover the entire range of parameters. Several studies have addressed the interesting problem of generalizing the Kramers rate formula to arbitrary barriers in the strong friction (Smoluchowski) limit. Closed-form expressions for the rate have been derived from exact solutions of the Smoluchowski equation [4,5,34] and by means of eigenmode expansions of particular bistable potentials [35,36]. A great deal of effort has been made to extend these strong-friction results to the spatial diffusion regime [25,26,29–31,37–48]. However, the accuracy of the proposed formulas is still not satisfactory for barriers of order k_BT which are important in physics and chemistry [31,48].

In this paper we propose a perturbation method for estimating the least nonvanishing eigenvalue of the Fokker–Planck equation, which combines the principal advantages of the two afore-mentioned approaches. This new method allows one to solve the pertinent eigenvalue problem systematically for any barrier height βE by taking into account both algebraic $[O(1/\beta E)]$ and exponential $[O(e^{-\beta E})]$ corrections. The reminder of the paper is organized as follows. In Sec. II, the Kramers problem is briefly outlined together with some preliminary results. A variational solution of this problem is presented in Sec. III. The solution is based on a Rayleigh quotient method, in which one varies the trial functions. An improved trial function is constructed from a perturbation theory that gives the Kramers trial function as zeroth-order approximation. The resulting rate formula, Eq. (3.20), whose derivation is given in Appendix A, involves an effective barrier frequency ω which is used as the variational parameter. A simple procedure to fix this parameter in the entire friction range is suggested in Sec. IV. The accuracy of our theoretical predictions is tested in Sec. V by comparing it with estimates of the rate from numerical calculations. The comparison also includes results from other variational rate expressions that are briefly reviewed in Appendix B. Section VI contains some final remarks.

II. PRELIMINARIES

Although conceptually the Kramers problem may be formulated in terms of the Langevin description [1,14] or its Hamiltonian equivalent [7,49], for the present purpose it will be convenient to employ the Fokker–Planck equation [1,4,5] (also called the Klein–Kramers equation) for the probability density $P(x,v,t)$ of finding the particle at the phase space point x,v

$$\partial_t P(x,v,t) = LP(x,v,t). \tag{2.1}$$

For a particle of unit mass the Fokker–Planck operator L reads

$$L = -v\frac{\partial}{\partial x} + U'(x)\frac{\partial}{\partial v} + \gamma\frac{\partial}{\partial v}\left(v + \beta^{-1}\frac{\partial}{\partial v}\right), \tag{2.2}$$

where $U'(x) = dU(x)/dx$, γ is the friction coefficient, and β the inverse energy available from the thermal bath, $\beta^{-1} = k_BT$. For simplicity the potential is assumed to be bounded from below $[U(x) \geqslant U_{\min} > -\infty]$ and unbounded from above $[U(x \to \pm\infty) \to +\infty]$, such that the stationary (equilibrium) solution of the Fokker–Planck equation, $LP_{\rm eq} = 0$, which is just the Maxwell–Boltzmann distribution

$$P_{\rm eq}(x,v) = (\beta/2\pi)^{1/2} Z^{-1} \exp\{-\beta[\tfrac{1}{2}v^2 + U(x)]\} \tag{2.3}$$

can be normalized

$$Z = \int_{-\infty}^{\infty} dx \exp[-\beta U(x)]. \tag{2.4}$$

In the spatial diffusion regime, for a potential with a parabolic barrier,

$$U(x) = U(0) - \tfrac{1}{2}\omega_b^2 x^2 + O(x^3), \quad \omega_b^2 = -U''(0), \tag{2.5}$$

the major Kramers result for the rate reads [1]

$$\Gamma_{\rm Kr} = \kappa \Gamma_{\rm TST}, \tag{2.6}$$

where $\Gamma_{\rm TST}$ follows from one-dimensional transition state theory (TST)

$$\Gamma_{\rm TST} = \frac{Z e^{-\beta U(0)}}{\sqrt{2\pi\beta} Z_- Z_+}, \tag{2.7}$$

$$Z_- = \int_{-\infty}^{0} dx \exp[-\beta U(x)], \quad Z_+ = \int_0^{\infty} dx \exp[-\beta U(x)],$$

and $\kappa = \sqrt{1 + \gamma^2/(4\omega_b^2)} - \gamma/(2\omega_b)$ is a transmission factor describing deviations from TST. It should be noted that Eq. (2.6) is asymptotic in the reduced barrier height, which is assumed to be large, $\beta E \gg 1$. In fact, this formula is nothing but the steepest-descent estimate to the rate, $\Gamma = \Gamma_{\rm Kr} + O[(\beta E)^{-1}]$, identical to approximating the full potential by its parabolic barrier part.

The problem of finite-barrier corrections to the Kramers rate has been actively studied in recent years and many different methods have been suggested for their evaluation [5,20,21,26,28–31,33–36,39,42–45,48]. A particular advance in this area can be attributed to Talkner [45]. Expanding the potential in powers of x as

$$U(x) \approx U(0) - \tfrac{1}{2}\omega_b^2 x^2 + \tfrac{1}{6}U'''x^3 + \tfrac{1}{24}U^{IV}x^4 \tag{2.8}$$

and combining a Rayleigh quotient method with a perturbation theory of Klosek, Matkowsky, and Schuss [33], Talkner derived explicit expressions for first- and second-order finite-barrier corrections which read

$$\Gamma_2^{\mathrm{FBC}}=\Gamma_{\mathrm{Kr}}\left\{1-\frac{U^{IV}}{8\beta\omega_b^4}\left(\frac{1-\kappa^2}{1+\kappa^2}\right)^2-\frac{1}{24\beta}\left(\frac{U'''}{\omega_b^3}\right)^2\left(\frac{1-\kappa^2}{1+\kappa^2}\right)^2\frac{10\kappa^4+41\kappa^2+10}{2\kappa^4+5\kappa^2+2}+\frac{1}{384}\left(\frac{U^{IV}}{\beta\omega_b^4}\right)^2\left(\frac{1-\kappa^2}{1+\kappa^2}\right)^4\times\left[35-\frac{16(30\kappa^6+103\kappa^4+70\kappa^2+12)}{(1-\kappa^2)(3\kappa^6+13\kappa^4+13\kappa^2+3)}\right]\right\}. \tag{2.9}$$

Clearly, Eqs. (2.6) and (2.9) are applicable only to potentials with parabolic barriers. Yet another common drawback is the neglect of ''exponentially small'' corrections, $O(e^{-\beta E})$, that are glossed over in the derivation of Eqs. (2.6) and (2.9). While these neglected corrections are indeed small for $\beta E\gg 1$, they do not differ much in magnitude from the ''leading'' algebraic corrections in the opposite low-barrier limit. A rough estimate telling when this neglect is adequate can be obtained by noting that the neglected exponential terms have to be smaller than (or at most of the same order as) the largest algebraic term, which here is the one of second order. This estimate gives $\beta E=6$. For lower barriers, one cannot expect that the algebraic corrections alone, Eq. (2.9), will necessarily improve the rate.

A strategy that will allow us to overcome the abovementioned drawbacks is to combine a variational (Rayleigh-quotient-based) method with a perturbation theory. For this purpose, we convert Eq. (2.1) to an eigenvalue problem by making the substitution $P(x,v,t)=P(x,v)e^{-\Gamma t}$ which gives

$$LP(x,v)=-\Gamma P(x,v). \tag{2.10}$$

The Fokker–Planck operator is not selfadjoint. Therefore, in order to derive a variational expression from which the rate Γ can be calculated, we also need an eigenfunction of the adjoint operator. With respect to the scalar product

$$\langle f|g\rangle=\int dxdv\,f(x,v)g(x,v), \tag{2.11}$$

the adjoint operator coincides with the backward operator

$$L^+=v\frac{\partial}{\partial x}-[U'(x)+\gamma v]\frac{\partial}{\partial v}+\frac{\gamma}{\beta}\frac{\partial^2}{\partial v^2}. \tag{2.12}$$

When one defines a scalar product weighted by the equilibrium distribution P_{eq}

$$(f,g)=\int dxdv\,P_{\mathrm{eq}}(x,v)f(x,v)g(x,v), \tag{2.13}$$

the adjoint operator L^* of L^+ is related to L by the expression $L^*=P_{\mathrm{eq}}^{-1}LP_{\mathrm{eq}}$. From detailed balance which holds for Brownian motion [4,5], L^* coincides with the backward operator of the time-reversed process

$$L^*=-v\frac{\partial}{\partial x}+[U'(x)-\gamma v]\frac{\partial}{\partial v}+\frac{\gamma}{\beta}\frac{\partial^2}{\partial v^2}. \tag{2.14}$$

Since L, L^+, and L^* have the same spectrum of eigenvalues [5,19], $-\Gamma$ also is the smallest nonvanishing eigenvalue of both adjoint operators L^+ and L^* with corresponding eigenfunctions h^+ and h, i.e.,

$$\begin{aligned}L^+h^+&=-\Gamma h^+,\\ L^*h&=-\Gamma h,\end{aligned} \tag{2.15}$$

where h^+ is the time-reversed function of h, $h^+(x,v)=h(x,-v)$, and $P(x,v)=h(x,v)P_{\mathrm{eq}}(x,v)$.

III. RAYLEIGH QUOTIENT METHOD

Since the Fokker–Planck operator is not self-adjoint, it is not obvious how a Rayleigh quotient identity for the pertinent eigenvalue has to be defined. Two different versions are currently used in the literature [12,26]. The starting point of our approach is the definition suggested by Moro and Polimeno [12] (see also Refs. [39,45])

$$\Gamma[h]=-\frac{(h^+,L^*h)}{(h^+,h)}. \tag{3.1}$$

Unlike the standard formulation of Rayleigh's quotient Eq. (B1), which is based on eigenfunctions of L and L^+ with the scalar product Eq. (2.11), the above definition, Eq. (3.1), involves eigenfunctions of the adjoint operators L^+ and L^*. These two operators act on the same space of phase-space (x,v) functions with finite second equilibrium moments. This is a much more general class of functions than those operated on by the original Fokker–Planck operator L, which must be absolutely integrable. It is therefore more convenient to deal with L^+ and L^* with the equilibrium weighted scalar product, Eq. (2.13) rather than with L and L^+. Additionally, an attractive feature of the Rayleigh quotient Eq. (3.1) is that it provides a variational formula in the entire friction range. An excellent exposition of this property may be found in our previous paper [50]. Note also that extensive use of the duality between L^+ and L^* has been made by Ryter [19] and Talkner [39,45] in order to calculate transition rates in bistable and metastable systems.

Perturbation theory

Clearly, Eq. (3.1) is an identity, i.e., given the true eigenfunction it yields the true eigenvalue. However, since $h(x,v)$ is not known exactly, we have to solve Eq. (2.15) by approximate methods to obtain a trial eigenfunction $\xi(x,v)$. Before proceeding two comments concerning $\xi(x,v)$ are in order. First, the desired trial function must be orthogonal on $h_0=1$, i.e.,

$$(\xi,1)=0, \tag{3.2}$$

because $h_0=1$ is an eigenfunction of L^* associated with eigenvalue $\lambda_0=0$. Second, almost all rate theories available for Fokker–Planck processes [1,17–30,32,33,35–47] are based on the remark that the barrier crossing rate Γ is expo-

nentially small and therefore may be neglected in the eigenvalue problem, Eq. (2.15), i.e.,

$$L^*\xi(x,v)=0. \tag{3.3}$$

However, neglect of the right hand side in Eq. (3.3) throws out exponential corrections to the rate which may be important for low barriers.

Here we present a systematic strategy how to go beyond this commonly used approximation, Eq. (3.3), and explicitly include exponential corrections to the rate into consideration. To this end, we split the full operator L^* into a leading contribution L_0^* and a correction L_1^* reading $L^*=L_0^*+L_1^*$, where

$$L_0^*=-v\frac{\partial}{\partial x}-(\omega^2x+\gamma v)\frac{\partial}{\partial v}+\frac{\gamma}{\beta}\frac{\partial^2}{\partial v^2} \tag{3.4}$$

describes the linear dynamics near the barrier, with an effective barrier frequency ω to be determined according to a variational principle, and

$$L_1^*=[U'(x)+\omega^2x]\frac{\partial}{\partial v} \tag{3.5}$$

the anharmonic correction. Based on this decomposition of the adjoint operator, a perturbation theory for the trial function can be performed leading to the series representation [33] (see also Refs. [45] and [21,30,36])

$$\xi(x,v)=\xi_0(x,v)+\xi_1(x,v)+\xi_2(x,v)+\cdots, \tag{3.6}$$

where $\xi_k(x,v)$ are determined recursively from the hierarchy of inhomogeneous equations

$$L_0^*\xi_k(x,v)=-(L_1^*+\Gamma_k)\xi_{k-1}(x,v),\quad k\geqslant 0, \tag{3.7}$$

with $\Gamma_0=0$ and $\xi_{-1}=0$. The result Γ_k contains all contributions to the rate up to order k in the perturbation L_1^*. It is obtained from a recurrence relation whose explicit form is found by insertion of Eq. (3.6) into Eq. (3.1) to be

$$\Gamma_{k+1}=\frac{1}{D_k}\left\{[D_{k-1}+(\xi_k^+,\xi_{k-1})]\Gamma_k+\sum_{i=0}^{k-2}2(\xi_k^+,\xi_i)\Gamma_{i+1}-(\xi_k,L_1^+\xi_{k-1}^+)-(\xi_k^+,L_1^*\xi_k)\right\}. \tag{3.8}$$

Here, D_k denotes the denominator of the Rayleigh quotient

$$D_k=(\xi_0^+,\cdots+\xi_k^+,\xi_0+\cdots+\xi_k). \tag{3.9}$$

The leading order term in the series, Eq. (3.6), satisfies the unperturbed (harmonic) problem

$$L_0^*\xi_0=0. \tag{3.10}$$

It is nothing but the Kramers' error function

$$\xi_0(x,v)=N_0+\mathrm{erf}[y(x,v)]=N_0+\frac{2}{\sqrt{\pi}}\int_0^{y(x,v)}dz\,\exp(-z^2),$$

$$y(x,v)=\sqrt{\frac{\beta}{2\gamma\mu}}(\mu v-\omega^2x), \tag{3.11}$$

$$\mu=\tfrac{1}{2}(\sqrt{4\omega^2+\gamma^2}-\gamma),$$

where the constant of integration N_0 is determined from Eq. (3.2). Using this lowest order approximation $\xi_0(x,v)$ we find for the rate Γ_1

$$\Gamma_1[\omega]=\frac{2\mu}{\pi ZD_0}\sqrt{\frac{\gamma+2\mu}{\gamma}}\int_{-\infty}^{\infty}dx\times\exp\left[-\beta U(x)-\beta\mu\frac{(\mu+\gamma)^2}{\gamma}x^2\right]. \tag{3.12}$$

The free parameter ω involved in Eq. (3.12) is fixed by minimizing $\Gamma_1[\omega]$.

Further corrections to the rate follow from the Rayleigh quotient when one uses the trial function including the first correction, $\xi(x,v)=\xi_0(x,v)+\xi_1(x,v)$. This latter correction is obtained from the equation

$$L_0^*\xi_1(x,v)=-(L_1^*+\Gamma_1)\xi_0(x,v). \tag{3.13}$$

Splitting off a Gaussian function from ξ_1,

$$\xi_1(x,v)=\sqrt{\frac{2\beta\mu}{\pi\gamma}}\exp[-y^2(x,v)]Q(x,v), \tag{3.14}$$

and using explicit expressions for L_1^* and ξ_0 brings Eq. (3.14) to the form

$$\left[-\mu-v\frac{\partial}{\partial x}+\left(\omega^2x-\frac{\omega^2+\mu^2}{\mu}v\right)\frac{\partial}{\partial v}+\frac{\gamma}{\beta}\frac{\partial^2}{\partial v^2}\right]Q(x,v)=-\omega^2x-U'(x)-\sqrt{\frac{\pi\gamma}{2\beta\mu}}\Gamma_1\exp[y^2(x,v)]\xi_0(x,v). \tag{3.15}$$

Since it is the barrier region that makes the dominant contribution to the integral in the numerator of the Rayleigh quotient Eq. (3.1), Eq. (3.15) can be solved systematically by expanding its right hand side in powers of x and v as

$$U'(x)\approx\sum_{m=1}^{n}(m+1)u_{m+1}x^m,$$

$$\exp(y^2)\xi_0\approx\sum_{m=0}^{n}Y_my^m. \tag{3.16}$$

Here, $u_m=U^{(m)}(0)/m!$, $Y_{2m}=N_0/m!$, $Y_{2m-1}=2^m/[\sqrt{\pi}(2m-1)!!]$, and y is defined in Eq. (3.11). Then, it is not difficult to show that the exact solution to the resulting equation

$$\left[-\mu - v\frac{\partial}{\partial x} + \left(\omega^2 x - \frac{\omega^2+\mu^2}{\mu}v\right)\frac{\partial}{\partial v} + \frac{\gamma}{\beta}\frac{\partial^2}{\partial v^2}\right]Q(x,v)$$

$$= -\omega^2 x - \sum_{m=1}^{n}(m+1)u_{m+1}x^m - \sqrt{\frac{\pi\gamma}{2\beta\mu}}\Gamma_1\sum_{m=0}^{n}Y_m\left(\frac{\beta}{2\gamma\mu}\right)^{m/2}(\mu v - \omega^2 x)^m \tag{3.17}$$

is just a polynomial of degree n

$$Q(x,v) = \sum_{m=0}^{n}\eta_m(x)v^m, \qquad \eta_m(x) = \sum_{j=0}^{n-m}\eta_{m,j}x^j, \tag{3.18}$$

whose coefficients $\eta_{m,j}$ follow from Eq. (3.17) by comparing like powers of x and v. Note that when acting on a polynomial in x and v the differential operator on the right hand side of Eq. (3.17) either reduces the degree of the polynomial by two or keeps it constant. Therefore, it is convenient to split $\eta_{m,j}$ into two subsets corresponding to even ($\eta_{m,j}$ with $m+j=2i$) and odd ($\eta_{m,j}$ with $m+j=2i-1$) coefficients which can then be evaluated separately. High efficiency is achieved by making use of computer algebra manipulators.

Hence, in first-order perturbation theory the trial function reads

$$\xi(x,v) = N_1 + \mathrm{erf}[y(x,v)] + \sqrt{\frac{2\beta\mu}{\pi\gamma}}\times\exp[-y^2(x,v)]\sum_{m=0}^{n}\sum_{j=0}^{n-m}\eta_{m,j}x^j v^m, \tag{3.19}$$

where the integration constant N_1 is again determined from Eq. (3.2). With this trial function, Eq. (3.19), the Rayleigh quotient yields in a straightforward way (for more details see Appendix A)

$$\Gamma_2[\omega] = \frac{2\mu}{\pi Z D_1}\sqrt{\frac{\gamma+2\mu}{\gamma}}\int_{-\infty}^{\infty}dx R(x)\times\exp\left[-\beta U(x) - \beta\mu\frac{(\mu+\gamma)^2}{\gamma}x^2\right], \tag{3.20}$$

where $R(x)$ is a known function, whose particular form depends on the truncation number n, Eqs. (A10) and (A14). Note that the above expression contains both exponential and algebraic corrections to the rate because we have neglected neither the right hand side of Eq. (2.15) nor L_1^*, respectively. Since Γ_k's are determined recursively from Eqs. (3.7) and (3.8), ω in Eq. (3.12) is fixed by minimization of $\Gamma_1[\omega]$, and Γ_1 is then kept constant while the free parameter ω is reevaluated to minimize $\Gamma_2[\omega]$, Eq. (3.20).

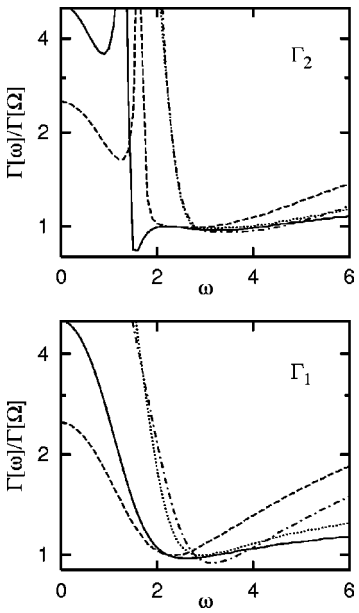

FIG. 1. Ratios $\Gamma_1[\omega]/\Gamma_1[\Omega]$, Eq. (3.12), and $\Gamma_2[\omega]/\Gamma_2[\Omega]$, Eq. (3.20), as functions of the free parameter ω for a double-well potential, Eq. (4.1). Solid lines, $\beta E=2$ and $\gamma/\Omega=1$; dashed lines, $\beta E=2$ and $\gamma/\Omega=10$; dotted lines, $\beta E=5$ and $\gamma/\Omega=1$; dot-dashed lines, $\beta E=5$ and $\gamma/\Omega=10$.

In closing it is important to note that any approach involving the Kramers trial function as zeroth-order approximation implicitly implies that the equilibration process is mainly determined by the immediate vicinity of the barrier top. The latter is a valid assumption as long as the rate of energy diffusion in the well is faster than the spatial diffusion rate across the barrier. In other words, both rate formulas obtained above, Eqs. (3.12) and (3.20), as well as those presented in Appendix B, are expected to work well only in the regime of moderate and large friction $\gamma \gtrsim \Omega$. Hereby we introduced an effective barrier frequency Ω,

$$\Omega = \beta^{(2-\alpha)/2\alpha}a^{1/\alpha}, \tag{3.21}$$

which is determined by the temperature and the order of the maximum and local strength of the potential in the vicinity of the top of the barrier

$$U(x) = U(0) - \frac{a}{\alpha}x^\alpha + \text{higher order terms.} \tag{3.22}$$

This frequency is given by the ratio between the thermal length scale of the potential, $(\beta a)^{-1/\alpha}$, and the thermal velocity $\beta^{-1/2}$. One can see that for a parabolic barrier it coincides with the barrier frequency $\Omega=\omega_b$.

IV. OPTIMAL CHOICE OF THE FREE PARAMETER

As already noted, an attractive feature of the Rayleigh identity Eq. (3.1), is that it is variational in the entire range of problem parameters. The latter is seen from Fig. 1 which shows the rate expressions $\Gamma_1[\omega]$ and $\Gamma_2[\omega]$ as functions of the free parameter ω for different values of γ/Ω and βE. The calculation is performed for a symmetric potential

$$U(x) = E[2(x/l)^6 - 3(x/l)^4], \tag{4.1}$$

which has two wells at $x=\pm l$ separated by a quartic barrier of height E and effective frequency $\Omega=l^{-1}(12E/\beta)^{1/4}$. Since the characteristic length l of the potential can always be absorbed into x, we set $l=1$ from here on. As evidenced by Fig. 1, the rate functionals Γ_1 and Γ_2 show a similar dependence on the variational parameter ω. Both vary from

$$\Gamma_k[0]=(\beta\gamma\langle x^2|P_{\rm eq}\rangle-1/\gamma)^{-1},\quad k=1,2, \tag{4.2}$$

through global minima, to the TST rate $\Gamma_{\rm TST}$, Eq. (2.7). This holds true at *all* barrier heights in the *entire* spatial diffusion regime, $\gamma/\Omega\gtrsim 1$ [51]. The only qualitative difference in the behavior of $\Gamma_1[\omega]$ and $\Gamma_2[\omega]$ is that besides the global minimum near $\omega=\Omega$ the rate functional $\Gamma_2[\omega]$ also exhibits a local minimum at low frequencies, $\omega<\Omega$.

It is thus seen that the free parameter ω can be determined by minimization of the corresponding rate functional. When applied to Eqs. (3.12) and (3.20), this results in self-consistent integral equations which must be solved numerically for ω at each value of the friction coefficient γ. Clearly, such a procedure will give the best approximation to the rate only if the Rayleigh quotient possesses a rigorous upper bound property. Otherwise, it will give a variational estimate, not an upper bound. Bounding properties of Eq. (3.1) have been studied in a previous paper [50]. We have found that a *sufficient* condition for the Rayleigh quotient to provide an upper bound to the exact rate, i.e., for $\Gamma[\xi]\geqslant\Gamma$, is that the spectrum of the Fokker–Planck operator be *real*. The latter is unconditionally valid in the limit of strong friction, $\gamma\gg\Omega$, where Eq. (2.2) reduces to a selfadjoint Smoluchowski operator. Unfortunately, outside of this strong friction (Smoluchowski) limit, there is no simple criterion for determining whether or not the spectrum of the Fokker–Planck operator is real. Therefore some approximation must be invoked to evaluate the difference $\Gamma[\xi]-\lambda_1$. An explicit expression for this difference is given by Eq. (2.30) in Ref. [50]. Since the main contribution to the series on the right-hand side of this equation comes from low lying eigenstates, one may write $\Gamma[\xi]-\lambda_1\approx(\xi^+,h_2)^2(\lambda_2-\lambda_1)$, where λ_2 is the second nonzero eigenvalue with associated eigenfunction h_2. Hence, a rough estimate for the value of γ below which the bounding properties of the Rayleigh quotient may be violated can be deduced just by studying the second nonzero eigenvalue λ_2. The latter is readily evaluated by making use of the harmonic approximation of the potential $U(x)$ near one of its minimum values, say, at $x=1$, $U(x)\approx U(1)+\frac{1}{2}\omega_w^2(x-1)^2$, where $\omega_w^2=U''(1)=24E$ is the frequency at the bottom of the well. This yields

$$\lambda_2\approx\tfrac{1}{2}(\gamma-\sqrt{\gamma^2-4\omega_w^2}), \tag{4.3}$$

from which it immediately follows that the Rayleigh quotient may lose its upper bound property for $\gamma\lesssim 2\omega_w$.

Proceeding further we note that the location of the global minimum of the rate functional, Eq. (3.20), is a function of all problem parameters, $\omega_2=\omega_2(\gamma,\beta,\{u_n\})$, where $\{u_n\}$ denotes the set of coefficients entering Kramers' problem through the potential $U(x)$. Therefore, ideally, one has to determine ω_2 by minimizing $\Gamma_2[\omega]$ for each particular set of parameters $(\gamma,\beta,\{u_n\})$. We have found, however, that the function $\omega_2(\gamma,\beta,\{u_n\})$ is rather insensitive to the friction coefficient γ (see Fig. 1). From this finding it immediately follows that the free parameter ω may be fixed in the entire friction range at once by setting $\omega=\omega_2^\infty$ where

$$\omega_2^\infty=\omega_2(\gamma\to\infty,\beta,\{u_n\}). \tag{4.4}$$

The same method of fixing ω is also applicable to the lowest order approximation $\Gamma_1[\omega]$. That is, in our calculations of $\Gamma_2[\omega_2^\infty]$ we set $\Gamma_1=\Gamma_1[\omega_1^\infty]$, where $\omega_1^\infty=\omega_1(\gamma\to\infty,\beta,\{u_n\})$.

Equations (3.20) and (4.4) constitute the principal result of this paper. The necessary calculation is easily performed by noting that in the strong friction limit, $\gamma\to\infty$, the Rayleigh quotient reduces to

$$\Gamma[\xi]=\frac{\int_{-\infty}^{\infty}dx\,\xi'^2(x)e^{-\beta U(x)}}{\beta\gamma\int_{-\infty}^{\infty}dx\,\xi^2(x)e^{-\beta U(x)}}. \tag{4.5}$$

For a sixth-order polynomial potential, Eq. (A11), within the perturbation theory with respect to the nonlinearity $U(x)+\omega^2x$, the trial function (up to and including the first-order correction) reads

$$\xi(x)=\sqrt{2\beta\omega^2/\pi}\left[\int_0^x dy e^{-\beta\omega^2y^2/2}+(\eta_{0,1}x+\eta_{0,3}x^3+\eta_{0,5}x^5)e^{-\beta\omega^2x^2/2}\right], \tag{4.6}$$

where

$$\eta_{0,1}=-\frac{1}{2}+\frac{11\gamma}{12\omega^2}\Gamma_1-\frac{u_2}{\omega^2}-\frac{3u_4}{\beta\omega^4}-\frac{15u_6}{\beta^2\omega^6},$$

$$\eta_{0,3}=\frac{5}{36}\beta\gamma\Gamma_1-\frac{u_4}{\omega^2}-\frac{5u_6}{\beta\omega^4}, \tag{4.7}$$

$$\eta_{0,5}=\frac{1}{90}\beta^2\gamma\Gamma_1\omega^2-\frac{u_6}{\omega^2}.$$

Note that for a symmetric potential the constant of integration is equal to zero independent of the order of approximation, i.e., $N_0=0$ and $N_1=0$.

In Table I and Fig. 2 we compare our theoretical predictions with the least nonvanishing eigenvalue computed numerically by using an improved reactive flux formula [50] and a high-accuracy path integral scheme [16]. As anticipated, the present method of fixing ω ($\Gamma_2[\omega_2^\infty]$) gives results that are almost indistinguishable from those obtained with $\Gamma_2[\omega_2]$. This holds true for all barrier heights and all values of the friction coefficient γ. Even in the worst case, $\beta E=1.25$ and $\gamma\sim\Omega$, the deviation between $\Gamma_2[\omega_2^\infty]$ and $\Gamma_2[\omega_2]$ is on the order of 1%.

It is also worth noticing that there is a rigorous upper bound property inherent to the Rayleigh quotient method throughout the moderate to strong friction range, $\gamma>2\omega_w$. We find that unlike the simplified rate formulas $\Gamma_1[\omega_1^\infty]$ and

TABLE I. Comparison between the Rayleigh quotient $\Gamma_2[\omega_2]$ obtained by minimization of Eq. (3.20) at each value of γ, the Rayleigh quotient $\Gamma_2[\omega_2^\infty]$ evaluated with the variational parameter ω fixed in the strong friction limit [Eqs. (3.20) and (4.4)], and the numerically exact results Γ for the least nonzero eigenvalue of the Fokker–Planck operator [Eqs. (2.2) and (4.1)]. Exponential notation $[-k]$ means that the number preceding is to be multiplied by 10^{-k}.

	$E=1.25$			$E=2.5$			$E=5$		
γ	$\Gamma_2[\omega_2]$	$\Gamma_2[\omega_2^\infty]$	Γ	$\Gamma_2[\omega_2]$	$\Gamma_2[\omega_2^\infty]$	Γ	$\Gamma_2[\omega_2]$	$\Gamma_2[\omega_2^\infty]$	Γ
1	0.3538	0.4194	0.2640	0.1416	0.1439	0.8976[−1]	0.1616[−1]	0.1685[−1]	0.1145[−1]
1.5	0.3202	0.3479	0.2802	0.1247	0.1258	0.9877[−1]	0.1490[−1]	0.1513[−1]	0.1246[−1]
2	0.2823	0.2965	0.2674	0.1109	0.1116	0.9805[−1]	0.1363[−1]	0.1372[−1]	0.1237[−1]
3	0.2219	0.2270	0.2210	0.8997[−1]	0.9040[−1]	0.8668[−1]	0.1150[−1]	0.1152[−1]	0.1117[−1]
4	0.1802	0.1824	0.1807	0.7512[−1]	0.7541[−1]	0.7417[−1]	0.9880[−2]	0.9886[−2]	0.9770[−2]
5	0.1506	0.1516	0.1510	0.6415[−1]	0.6433[−1]	0.6381[−1]	0.8615[−2]	0.8617[−2]	0.8571[−2]
6	0.1289	0.1294	0.1290	0.5576[−1]	0.5586[−1]	0.5559[−1]	0.7610[−2]	0.7611[−2]	0.7589[−2]
7	0.1123	0.1126	0.1123	0.4918[−1]	0.4923[−1]	0.4907[−1]	0.6797[−2]	0.6798[−2]	0.6786[−2]
8	0.9945[−1]	0.9959[−1]	0.9937[−1]	0.4390[−1]	0.4393[−1]	0.4381[−1]	0.6129[−2]	0.6130[−2]	0.6122[−2]
9	0.8910[−1]	0.8919[−1]	0.8898[−1]	0.3959[−1]	0.3961[−1]	0.3952[−1]	0.5573[−2]	0.5574[−2]	0.5568[−2]
10	0.8065[−1]	0.8072[−1]	0.8051[−1]	0.3602[−1]	0.3603[−1]	0.3596[−1]	0.5103[−2]	0.5104[−2]	0.5100[−2]
15	0.5451[−1]	0.5453[−1]	0.5438[−1]	0.2467[−1]	0.2467[−1]	0.2464[−1]	0.3564[−2]	0.3564[−2]	0.3562[−2]
20	0.4107[−1]	0.4109[−1]	0.4098[−1]	0.1869[−1]	0.1869[−1]	0.1867[−1]	0.2723[−2]	0.2723[−2]	0.2721[−2]
30	0.2747[−1]	0.2747[−1]	0.2741[−1]	0.1255[−1]	0.1255[−1]	0.1254[−1]	0.1841[−2]	0.1841[−2]	0.1840[−2]
60	0.1375[−1]	0.1375[−1]	0.1373[−1]	0.6307[−2]	0.6307[−2]	0.6300[−2]	0.9291[−3]	0.9291[−3]	0.9284[−3]
80	0.1032[−1]	0.1032[−1]	0.1030[−1]	0.4733[−2]	0.4733[−2]	0.4728[−2]	0.6977[−3]	0.6977[−3]	0.6972[−3]
100	0.8256[−2]	0.8256[−2]	0.8246[−2]	0.3787[−2]	0.3787[−2]	0.3784[−2]	0.5585[−3]	0.5585[−3]	0.5581[−3]
1000	0.8254[−3]	0.8254[−3]	0.8248[−3] [a]	0.3789[−3]	0.3789[−3]	0.3786[−3] [a]	0.5591[−4]	0.5591[−4]	0.5587[−4] [a]

[a]Exact estimate of the eigenvalue calculated from the respective Smoluchowski equation.

$\Gamma_2[\omega_2^\infty]$ which usually overestimate the exact rate in the entire friction range, the true Rayleigh quotient estimates $\Gamma_1[\omega_1]$ and $\Gamma_2[\omega_2]$ may drop below Γ for $\gamma \lesssim 2\omega_w$ (see Fig. 2). This result is in full agreement with our previous observation that the Rayleigh quotient may lose its upper bound property when the spectrum of the Fokker–Planck operator becomes complex [see Eq. (4.3) and the discussion above it]. With further decreasing γ, however, Eqs. (3.12) and (3.20) rapidly restore their bounding properties despite the fact that the spectrum is no longer real. This is because the true rate Γ falls off with the friction coefficient when $\gamma < \Omega$, while the Rayleigh quotient estimates, Eqs. (3.12) and (3.20), approach in the limit of weak friction the TST rate $\Gamma_{\rm TST}$, Eq. (2.7).

Most importantly, however, is the result that the range of applicability of the present perturbation method is quite robust to variations in the barrier height. One would expect the accuracy of Eq. (3.20) to fall off quickly as βE went down and $\Gamma \to O(1)$, but in fact going from a potential with $\beta E = 5$ to one about $\beta E = 1.25$, there was almost no decay in the accuracy of the results over a broad range of γ. Even at the smallest value of βE the proposed rate formula $\Gamma_2[\omega_2^\infty]$ is seen to provide an accuracy of 0.3% for $\gamma \gtrsim 3\ \Omega$. Larger deviations are observed for γ values on the order Ω and lower. These deviations arise because the slow energy diffusion process, which causes the rate to fall off with decreasing γ, is not accounted for by the present splitting of the adjoint operator, Eqs. (3.4) and (3.5). This splitting results in the Kramers-like trial function, Eqs. (3.11) and (3.19), which is a poor approximation to the true eigenfunction $h(x,v)$ when energy-diffusion effects appear.

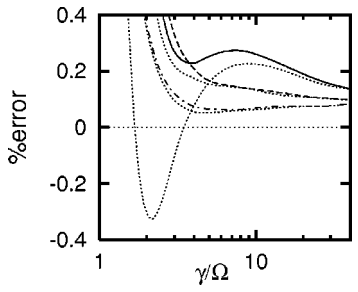

FIG. 2. Percentage errors, $100\times$(approximate − exact)/exact, in the least nonvanishing eigenvalue of the Fokker–Planck operator, Eqs. (2.2) and (4.1), made by using $\Gamma_2[\omega_2^\infty]$, Eqs. (3.20) and (4.4). Solid, dashed, and dot-dashed lines are for $\beta E = 1.25$, 2.5, and 5, respectively. Dotted lines are for results obtained with $\Gamma_2[\omega_2]$ [that is, by minimization of Eq. (3.20) at each value of γ].

V. COMPARISON WITH OTHER VARIATIONAL APPROACHES

In this section we compare the efficacy of our method with that of two other variational approaches commonly used in the literature. One is based on the standard definition of Rayleigh's quotient suggested by Larson and Kostin [26]. The other is variational TST (VTST) [2,7,40–42,44,46]. Both approaches are briefly outlined in Appendix B. The corresponding rate expressions $\Gamma_1^{\rm LK}[\omega]$ and $\Gamma_{\rm VTST}[\omega]$ are given by Eqs. (B2) and (B3), respectively.

To begin with, we show in Fig. 3 these expressions as functions of the variational parameter ω. The calculation is performed for the symmetric double-well potential, Eq. (4.1). One sees that both approaches fail to provide a variational formula in the entire parameter space. The standard Rayleigh

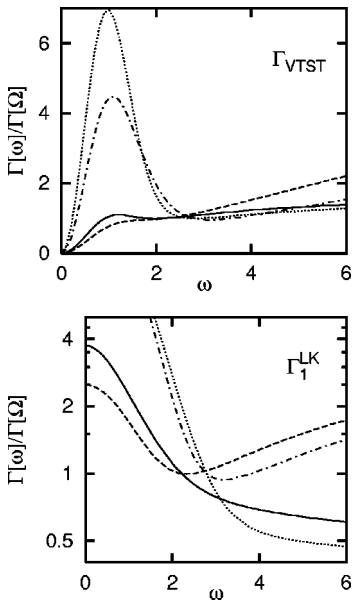

FIG. 3. Same as in Fig. 1 but for Γ_{VTST}, Eq. (B3), and Γ_1^{LK}, Eq. (B2).

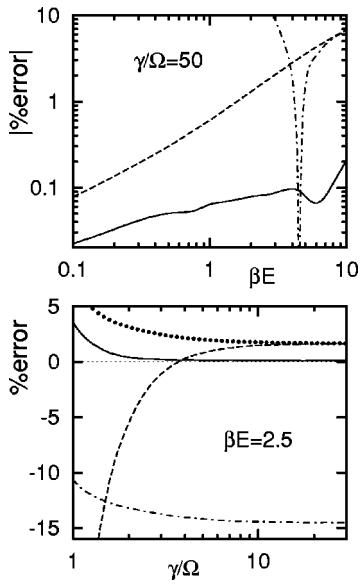

FIG. 4. Percentage errors in the least nonvanishing eigenvalue of the Fokker–Planck operator, Eqs. (2.2) and (4.1), made by using different rate formulas. Solid lines are for the present expression $\Gamma_2[\omega_2^\infty]$, Eqs. (3.20) and (4.4). Circles, dashed, and dot-dashed lines are for results obtained by minimization of Γ_1 [Eq. (3.12)], Γ_1^{LK} [Eq. (B2)], and Γ_{VTST} [Eq. (B3)], respectively.

quotient $\Gamma_1^{\mathrm{LK}}[\omega]$ shows a minimum for $\gamma \gg \Omega$, in which case it reduces to $\Gamma_1[\omega]$. Outside of this strong friction limit, the rate functional $\Gamma_1^{\mathrm{LK}}[\omega]$ does *not* necessarily exhibit a nontrivial minimum and may be a monotonic function of ω. Analogously, the VTST rate functional Eq. (B3), is in general variational only for moderate and high barriers, $\beta E \gtrsim 3$. As seen from Fig. 3, when the variational parameter increases, $\Gamma_{\mathrm{VTST}}[\omega]$ increases to a local maximum followed by a local minimum if the barrier is high, whereas it increases only monotonically for low barriers. This low-barrier problem may in principle be resolved by making use of curved dividing surfaces that are computed numerically from Hamilton's equations of motion for an effective two degrees of freedom Hamiltonian [41]. In such a case, the VTST method reduces to running classical trajectories and looking for that orbit whose classical action is minimal with the additional constraint that the configuration space path of the orbit is a ''good'' dividing surface. Since the required numerical procedure is rather arduous, we will not do so here.

In Fig. 4 we compare the relative errors made by the various approximations for the least nonvanishing eigenvalue discussed in this paper. It is immediately apparent that the best agreement with exact rates is obtained with the present formula $\Gamma_2[\omega_2^\infty]$, Eq. (3.20). Its accuracy deteriorates only slowly varying from 0.01% for $\beta E = 0.1$ to 0.1% for $\beta E = 10$. This seemingly surprising result that the error increases with increasing barrier height is actually not surprising. Recall that the Kramers-like trial function [Eq. (3.19)] underlying Eq. (3.20) is based on a harmonic approximation of the potential, Eq. (3.4). The latter leads to a poor approximation to the true eigenfunction $h(x,v)$ when the anharmonicity of the potential near the barrier top becomes strong. It is noteworthy that the other rate formulas show the same kind of behavior in the sense that their accuracy also deteriorates with increasing barrier height. However, the corresponding errors are larger by orders of magnitude than the error made by using Eq. (3.20). As anticipated, the first-order approximations Γ_1 and Γ_1^{LK} based on two different Rayleigh's identities [Eqs. (3.1) and (B1), respectively] coincide in the limit of strong friction, $\gamma \gtrsim 10\ \Omega$. For moderate friction the situation becomes different. In this case, the standard Rayleigh quotient Γ_1^{LK} gives results that abruptly drop below the true rate for $\gamma < 2\omega_w$. In contrast, the accuracy of Γ_1 remains almost constant in the spatial diffusion regime. The VTST rate expression, Eq. (B3), is seen to be the least accurate. In fact, we find that Γ_{VTST} does not give satisfactory results for the quartic-barrier potential Eq. (4.1) anywhere except $\beta E \approx 5$ when it happens to coincide with the true rate. In the limit of large barriers, $\beta E \gtrsim 10$, the VTST rate expression overestimates the true rate by the same amount as Γ_1 and Γ_1^{LK}, while for moderate and low barriers, $\beta E < 4$, it underestimates the exact result by more than 10%.

As a second example, we consider a potential with asymmetric nonlinearity about the barrier which reads

$$U(x) = \frac{E}{3+2\alpha}[3x^4 + 4\alpha x^3 - 6(1+\alpha)x^2]. \qquad (5.1)$$

Here, we set the characteristic length $l = 1$, and α is an asymmetry parameter. The potential has two wells at $x = +1$ and $-1-\alpha$ of depth $U(1) = -E$ and $U(-1-\alpha) = -E(3+\alpha)(1+\alpha)^3/(3+2\alpha)$, respectively, separated by a parabolic barrier at $x = 0$ of frequency $\omega_b^2 = 12E(1+\alpha)/(3+2\alpha)$.

First we tackle the symmetric case $\alpha = 0$. The corresponding results are shown in Fig. 5. The logarithmic plot clearly demonstrates that the present theory substantially improves the first-order Rayleigh quotient estimate Γ_1, Eq. (3.12), *systematically* reducing the error by 1 order of magnitude. We again find that the errors are rather insensitive to the friction coefficient γ, being nearly constant across the spatial diffusion regime, i.e., for all $\gamma \gtrsim 2\omega_w = \sqrt{8}\,\omega_b$. However, unlike

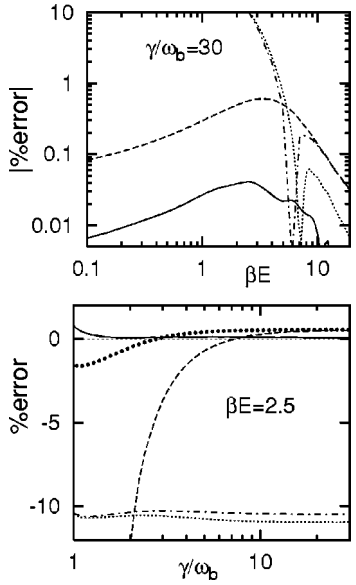

FIG. 5. Same as in Fig. 4 but for the potential, Eq. (5.1), with $\alpha=0$. Dotted lines are for Γ_2^{FBC}, Eq. (2.9).

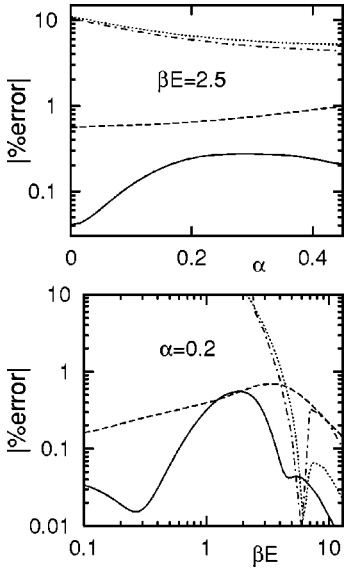

FIG. 6. Same as in Fig. 5 but for an asymmetric double-well potential, Eq. (5.1) with $\alpha\neq 0$.

the case of quartic barrier considered above, for a parabolic barrier the theory works well at all values of the reduced barrier height including both limits of high ($\beta E\to 0$) and vanishing ($\beta E\to\infty$) temperature. Note that in the latter limit it becomes exact. With the present rate formula $\Gamma_2[\omega_2^\infty]$, a maximal error of 0.04% is attained in the spatial diffusion regime for $\beta E=2.5$. This is in contrast to the second-order finite-barrier expansion Γ_2^{FBC}, Eq. (2.9), which considerably underestimates the rate for $\beta E<5$. As seen in Fig. 5, its relative error increases *exponentially* with decreasing barrier height and very soon grows out of the scale of the figure, a clear indication of the importance of the neglected exponential corrections. The same holds true for VTST, whose error is large compared to those of the other approaches.

Finally, we consider an asymmetric double-well potential, Eq. (5.1) with $\alpha\neq 0$. The corresponding relative errors as functions of α and βE are shown in Fig. 6 for $\gamma/\omega_b=30$. It is seen that the present rate formula $\Gamma_2[\omega_2^\infty]$ is in good agreement with the exact numerical results. However, this agreement is somewhat worse than in the symmetric case. The discrepancy is most pronounced for $\alpha=0.2$ and $\beta E\approx 1.5$ in which case the first- and second-order Rayleigh quotient formulas (Γ_1 and Γ_2) overestimate the true rate by the same amount of 0.5%. Away from this region the second-order formula is considerably better than Γ_1. The VTST rate Γ_{VTST} [Eq. (B3)] and second-order finite-barrier expansion Γ_2^{FBC} [Eq. (2.9)] are again much less accurate. Indeed, their relative errors are by orders of magnitude larger than the error made by using Eq. (3.20). This holds true at all values of the problem parameters α, βE, and γ except when Γ_{VTST} and Γ_2^{FBC} happen to coincide with the true rate.

VI. CONCLUSIONS

This paper was written with three objectives in mind. First we have compared the relative abilities of different variational methods to precisely predict the rate of thermally activated barrier crossing processes in condensed media. These abilities have already been examined in a number of studies [43,46–48]. However, the corresponding analyses have been restricted either to the extreme limit of high barriers [46,47] or to one (either VTST or Rayleigh quotient) method [12,26,43,48]. Here we have compared different variational expressions for the rate in different kinds of potentials over a broad range of problem parameters. The second purpose of this work was to point out an approximation that has been almost universally made in all known rate theories. The approximation consists of neglecting exponentially small contributions to the rate. We showed that the neglect of these exponential corrections may introduce large errors in the limit of moderate and low barriers.

The final and primary goal of this paper was to develop a perturbation method which *systematically* accounts for *both* the algebraic and the exponential corrections. The resulting rate expression produces unprecedentedly accurate results at all barrier heights and for the whole friction range in the spatial diffusion regime. For potentials with nonparabolic barriers the accuracy of the method can be further improved if one employs as zeroth-order approximation, instead of Eq. (3.11), a non-Kramers trial function suggested in Ref. [25]. Although we restricted our consideration to the spatial diffusion regime of a Markovian one-dimensional activated rate process, the methods can be applied to the case of memory friction, as well as to systems with more than one degree of freedom. A similar method can also be developed for the limit of underdamped Brownian motion [33], in which case finite-barrier corrections to the rate are known to be larger than in the spatial diffusion regime [12,13,25,30,31].

ACKNOWLEDGMENTS

The author gratefully acknowledges Susan C. Tucker for advice and enlightening discussions. This work was supported by the National Science Foundation under Grant No. CHE-9727361.

APPENDIX A

In this Appendix we outline the derivation of the central result of this paper as given in Eq. (3.20). With Eq. (3.8) the Rayleigh quotient Γ_2, which includes second- and higher-order corrections in the nonlinearity $U'(x)+\omega^2 x$, reads

$$\Gamma_2=\frac{(\xi^+_{0(n)},\xi_1)\Gamma_1-(\xi^+_0,L_1^*\xi_0)-(\xi_1,L_1^+\xi^+_0)-(\xi^+_1,L_1^*\xi_1)}{D_1}, \tag{A1}$$

where we have used $(\xi_{0(n)},\xi^+_1)=(\xi^+_{0(n)},\xi_1)$. The function $\xi_{0(n)}$ appearing in Eq. (A1) is an approximation to the Kramers function ξ_0 obtained by truncating its series representation according to Eq. (3.16), i.e.,

$$\xi_0\approx\xi_{0(n)}=N_0+\frac{e^{-y^2}}{\sqrt{\pi}}\sum_{m=1}^{[(n+1)/2]}\frac{2^m y^{2m-1}}{(2m-1)!!}. \tag{A2}$$

In the above, $[(n+1)/2]$ denotes the integer part of $\frac{1}{2}(n+1)$. The v integrals in the numerator of Eq. (A1) can be eliminated by noting that the corresponding integrands are just a product of a polynomial in v with a Gaussian function that has a zero mean $\langle\langle v\rangle\rangle=0$ and variance $\langle\langle v^2\rangle\rangle=\sigma$,

$$\sigma=\frac{\gamma}{\beta(\gamma+2\mu)}. \tag{A3}$$

Therefore, it is convenient to write down $\xi^+_{0(n)}$ in the form

$$\xi^+_{0(n)}(x,v)=-\sqrt{\frac{2\beta}{\pi\gamma\mu}}\exp\left[-\frac{\beta(\mu v+\omega^2 x)^2}{2\gamma\mu}\right]\times\sum_{m=0}^{2[(n+1)/2]-1}\psi_m(x)v^m, \tag{A4}$$

$$\psi_m(x)=\sum_{j=1}^{[(n+1)/2]-[m/2]}\frac{(2j-1)!\beta^{j-1}\mu^m(\omega^2 x)^{2j-1-m}}{m!(2j-1-m)!(2j-1)!!(\gamma\mu)^{j-1}}.$$

Analogously,

$$L_1^*\xi_1(x,v)=\sqrt{\frac{2\beta\mu}{\pi\gamma}}[U'(x)+\omega^2 x]\times\exp\left[-\frac{\beta(\mu v-\omega^2 x)^2}{2\gamma\mu}\right]\sum_{m=0}^{n+1}\varphi_m(x)v^m, \tag{A5}$$

where the functions $\varphi_m(x)$ are expressed in terms of $\eta_m(x)$, Eq. (3.18), by the relation

$$\varphi_m=(m+1)\eta_{m+1}+\frac{\beta}{\gamma}(\omega^2 x\eta_m-\mu\eta_{m-1}),\quad 0\leqslant m\leqslant n+1, \tag{A6}$$

with $\eta_{-1}=\eta_{n+1}=\eta_{n+2}=0$. Then, the Gaussian integrals over v in the numerator of Eq. (A1) are easily performed analytically to yield Eq. (3.20), where the function $R(x)$ is determined in terms of $\eta_m(x)$, $\psi_m(x)$, and $\varphi_m(x)$. Its particular form depends on the potential $U(x)$, or more precisely, on the degree n of its polynomial approximation, Eq. (3.16).

In our subsequent calculation we will be more specific, considering two explicit cases of polynomial potentials that cover both applications in Secs. IV and V, Eqs. (4.1) and (5.1). First, we tackle an asymmetric cubic-quartic potential of the form

$$U(x)=u_2x^2+u_3x^3+u_4x^4, \tag{A7}$$

which has been extensively studied by many authors within this context (see, e.g., Refs. [26,28–30,35,39,44,45]). In that event, the exact solution to Eq. (3.17) reads

$$Q(x,v)=\eta_{0,0}+\eta_{0,1}x+\eta_{1,0}v+\eta_{0,2}x^2+\eta_{1,1}vx+\eta_{2,0}v^2+\eta_{0,3}x^3+\eta_{1,2}vx^2+\eta_{2,1}v^2x+\eta_{3,0}v^3, \tag{A8}$$

where the coefficients $\eta_{m,j}$ are found to be

$$\eta_{0,0}=\sqrt{\frac{\pi\gamma}{2\beta\mu^3}}N_0\Gamma_1+\frac{2\gamma}{\beta\mu}\eta_{2,0},$$

$$\eta_{0,2}=-\sqrt{\frac{\pi\beta}{32\gamma\mu}}(3\omega^2+2\mu^2)N_0\Gamma_1+\mu^{-2}(\omega^4+\tfrac{9}{2}\omega^2\mu^2+3\mu^4)\eta_{2,0},$$

$$\eta_{1,1}=\sqrt{\frac{\pi\beta\mu}{8\gamma}}N_0\Gamma_1-\mu^{-1}(2\omega^2+3\mu^2)\eta_{2,0},$$

$$\eta_{2,0}=\sqrt{\frac{\pi\beta}{72\gamma\mu}}N_0\Gamma_1+\frac{2u_3\mu}{2\omega^4+5\omega^2\mu^2+2\mu^4},$$

$$\eta_{0,1}=\frac{-\beta(3\omega^4+\omega^2\mu^2-4\mu^4)\Gamma_1+3\beta\mu(\omega^2+2u_2)(\omega^2+2\mu^2)-6\gamma(3\omega^4+7\omega^2\mu^2+8\mu^4)\eta_{3,0}}{6\beta\mu^2(\omega^2+\mu^2)},$$

$$\eta_{1,0}=\frac{\beta(3\omega^2+\mu^2)\Gamma_1-3\beta\mu(\omega^2+2u_2)+6\gamma(3\omega^2+7\mu^2)\eta_{3,0}}{6\beta\mu(\omega^2+\mu^2)},$$

$$\eta_{0,3}=\frac{\beta(11\omega^4+17\omega^2\mu^2+6\mu^4)}{18\gamma\mu}\Gamma_1-\frac{3\omega^6+22\omega^4\mu^2+34\omega^2\mu^4+12\mu^6}{3\mu^3}\eta_{3,0},$$

$$\eta_{1,2}=-\frac{\beta(5\omega^2+3\mu^2)}{6\gamma}\Gamma_1+\frac{3\omega^4+10\omega^2\mu^2+6\mu^4}{\mu^2}\eta_{3,0},$$

$$\eta_{2,1}=\frac{\beta\mu}{3\gamma}\Gamma_1-\frac{3\omega^2+4\mu^2}{\mu}\eta_{3,0},$$

$$\eta_{3,0}=\frac{\beta}{12\gamma}\Gamma_1-\frac{3u_4\mu^2}{3\omega^6+13\omega^4\mu^2+13\omega^2\mu^4+3\mu^6}. \tag{A9}$$

With this particular solution the function $R(x)$ is found to be

$$\begin{aligned}R=1&-(\beta^2/\gamma)\sigma\{(U'+\omega^2x)[\eta_0(1+\varphi_0)\\&+\sigma(\eta_2+\eta_2\varphi_0-\eta_1\varphi_1+\eta_0\varphi_2)\\&+3\sigma^2(-\eta_3\varphi_1+\eta_2\varphi_2-\eta_1\varphi_3\\&+\eta_0\varphi_4)+15\sigma^3(-\eta_3\varphi_3+\eta_2\varphi_4)]\\&-(\Gamma_1/\mu)[\eta_0\psi_0+\sigma(\eta_2\psi_0+\eta_1\psi_1+\eta_0\psi_2)\\&+3\sigma^2(\eta_3\psi_1+\eta_2\psi_2+\eta_1\psi_3)+15\sigma^3\eta_3\psi_3]\}.\end{aligned} \tag{A10}$$

As a second example, we consider the case of a symmetric potential

$$U(x)=u_2x^2+u_4x^4+u_6x^6, \tag{A11}$$

which results in

$$\begin{aligned}Q(x,v)=&\eta_{0,1}x+\eta_{1,0}v+\eta_{0,3}x^3+\eta_{1,2}vx^2+\eta_{2,1}v^2x\\&+\eta_{3,0}v^3+\eta_{0,5}x^5+\eta_{1,4}vx^4+\eta_{2,3}v^2x^3\\&+\eta_{3,2}v^3x^2+\eta_{4,1}v^4x+\eta_{5,0}v^5,\end{aligned} \tag{A12}$$

with the coefficients given by

$$\eta_{0,1}=-\frac{3\omega^4+\omega^2\mu^2-4\mu^4}{6\mu^2(\omega^2+\mu^2)}\Gamma_1-\frac{\gamma(3\omega^4+7\omega^2\mu^2+8\mu^4)}{\beta\mu^2(\omega^2+\mu^2)}\eta_{3,0}+\frac{20\gamma^2(\omega^2+2\mu^2)}{\beta^2\mu(\omega^2+\mu^2)}\eta_{5,0}+\frac{(2u_2+\omega^2)(\omega^2+2\mu^2)}{2\mu(\omega^2+\mu^2)},$$

$$\eta_{1,0}=\frac{3\omega^2+\mu^2}{6\mu(\omega^2+\mu^2)}\Gamma_1+\frac{\gamma(3\omega^2+7\mu^2)}{\beta\mu(\omega^2+\mu^2)}\eta_{3,0}-\frac{20\gamma^2}{\beta^2(\omega^2+\mu^2)}\eta_{5,0}-\frac{2u_2+\omega^2}{2(\omega^2+\mu^2)},$$

$$\eta_{0,3}=\frac{\beta}{90\gamma\mu}(55\omega^4+19\omega^2\mu^2-24\mu^4)\Gamma_1-\frac{1}{3\mu^3}(3\omega^6+22\omega^4\mu^2+34\omega^2\mu^4+12\mu^6)\eta_{3,0}$$

$$+\frac{\gamma}{3\beta\mu^2}(110\omega^4+368\omega^2\mu^2+222\mu^4)\eta_{5,0},$$

$$\eta_{1,2}=-\frac{\beta}{30\gamma}(25\omega^2+3\mu^2)\Gamma_1+\frac{1}{\mu^2}(3\omega^4+10\omega^2\mu^2+6\mu^4)\eta_{3,0}-\frac{\gamma}{\beta\mu}(50\omega^2+66\mu^2)\eta_{5,0},$$

$$\eta_{2,1}=\frac{\beta\mu}{3\gamma}\Gamma_1-\frac{1}{\mu}(3\omega^2+4\mu^2)\eta_{3,0}+20\frac{\gamma}{\beta}\eta_{5,0},$$

$$\eta_{3,0}=\frac{\beta(30\omega^6+36\omega^4\mu^2-90\omega^2\mu^4-64\mu^6)}{120\gamma(3\omega^6+13\omega^4\mu^2+13\omega^2\mu^4+3\mu^6)}\Gamma_1+\frac{\gamma(30\omega^6+271\omega^4\mu^2+460\omega^2\mu^4+171\mu^6)\eta_{5,0}-6\beta u_4\mu^3}{2\beta\mu(3\omega^6+13\omega^4\mu^2+13\omega^2\mu^4+3\mu^6)},$$

$$\eta_{0,5}=\frac{\beta^2}{900\gamma^2\mu^2}(137\omega^8+512\omega^6\mu^2+707\omega^4\mu^4+372\omega^2\mu^6+60\mu^8)\Gamma_1$$

$$-\frac{1}{10\mu^5}(10\omega^{10}+137\omega^8\mu^2+512\omega^6\mu^4+707\omega^4\mu^6+372\omega^2\mu^8+60\mu^{10})\,\eta_{5,0},$$

$$\eta_{1,4}=-\frac{\beta^2}{180\gamma^2\mu}(77\omega^6+170\omega^4\mu^2+131\omega^2\mu^4+30\mu^6)\Gamma_1+\frac{1}{2\mu^4}(10\omega^8+77\omega^6\mu^2+170\omega^4\mu^4+131\omega^2\mu^6+30\mu^8)\,\eta_{5,0},$$

$$\eta_{2,3}=\frac{\beta^2}{90\gamma^2}(47\omega^4+59\omega^2\mu^2+20\mu^4)\Gamma_1-\frac{1}{\mu^3}(10\omega^6+47\omega^4\mu^2+59\omega^2\mu^4+20\mu^6)\,\eta_{5,0},$$

$$\eta_{3,2}=-\frac{\beta^2\mu}{30\gamma^2}(9\omega^2+5\mu^2)\Gamma_1+\frac{1}{\mu^2}(10\omega^4+27\omega^2\mu^2+15\mu^4)\,\eta_{5,0},$$

$$\eta_{4,1}=\frac{\beta^2\mu^2}{15\gamma^2}\Gamma_1-\frac{1}{\mu}(5\omega^2+6\mu^2)\,\eta_{5,0},$$

$$\eta_{5,0}=\frac{\beta^2\mu}{90\gamma^2}\Gamma_1-\frac{10u_6\mu^4}{10\omega^{10}+87\omega^8\mu^2+227\omega^6\mu^4+227\omega^4\mu^6+87\omega^2\mu^8+10\mu^{10}}. \tag{A13}$$

In this case, the function $R(x)$ takes the form

$$R=1-(\beta^2/\gamma)\sigma\{(U'+\omega^2x)[\eta_0(1+\varphi_0)+\sigma(\eta_2+\eta_2\varphi_0-\eta_1\varphi_1+\eta_0\varphi_2)+3\sigma^2(\eta_4+\eta_4\varphi_0-\eta_3\varphi_1+\eta_2\varphi_2-\eta_1\varphi_3+\eta_0\varphi_4)$$
$$+15\sigma^3(-\eta_5\varphi_1+\eta_4\varphi_2-\eta_3\varphi_3+\eta_2\varphi_4-\eta_1\varphi_5+\eta_0\varphi_6)+105\sigma^4(-\eta_5\varphi_3+\eta_4\varphi_4-\eta_3\varphi_5+\eta_2\varphi_6)+945\sigma^5(-\eta_5\varphi_5$$
$$+\eta_4\varphi_6)-(\Gamma_1/\mu)[\eta_0\psi_0+\sigma(\eta_2\psi_0+\eta_1\psi_1+\eta_0\psi_2)+3\sigma^2(\eta_4\psi_0+\eta_3\psi_1+\eta_2\psi_2+\eta_1\psi_3+\eta_0\psi_4)+15\sigma^3(\eta_5\psi_1+\eta_4\psi_2$$
$$+\eta_3\psi_3+\eta_2\psi_4+\eta_1\psi_5)+105\sigma^4(\eta_5\psi_3+\eta_4\psi_4+\eta_3\psi_5)+945\sigma^5\eta_5\psi_5]\}. \tag{A14}$$

APPENDIX B

In this Appendix, we briefly outline two other variational approaches to Kramers' problem that have been frequently used in the past to calculate rates in the spatial diffusion regime. An expression for the least nonvanishing eigenvalue of the Fokker–Planck equation, which is a straightforward generalization of the Rayleigh–Ritz quotient for the ground state of a selfadjoint operator, was proposed by Larson and Kostin [26] (see also Refs. [20,38]),

$$\Gamma^{\mathrm{LK}}[h]=-\frac{\langle h|LP\rangle}{\langle h|P\rangle}=\frac{\frac{\gamma}{\beta}\left(\frac{\partial h}{\partial v},\frac{\partial h}{\partial v}\right)}{(h,h)}. \tag{B1}$$

We used the subscript LK in the above definition to distinguish it from that of Moro and Polimeno, Eq. (3.1). Substitution of the Kramers trial function, Eq. (3.11), into Eq. (B1) yields the following expression for the rate:

$$\Gamma_1^{\mathrm{LK}}[\omega]=\frac{2\mu}{\pi Z}\sqrt{\frac{\gamma}{\gamma+2\mu}}\int_{-\infty}^{\infty}dx\exp\Big[-\beta U(x)$$
$$-\beta\mu\frac{(\mu+\gamma)^2}{\gamma+2\mu}x^2\Big]\Big/(\xi_0,\xi_0). \tag{B2}$$

In Secs. IV and V, we refer to Eq. (B1) as the standard Rayleigh quotient method.

Another very different variational approach is based on the transformation of the original Fokker–Planck dynamics to an equivalent infinite dimensional Hamiltonian system [49]. Within the Hamiltonian formulation the forward (backward) rate constant Γ_f (Γ_b) may be estimated, by means of multidimensional TST, as a ratio of the equilibrium unidirectional flux through some chosen dividing surface to the population of the reactant (product) well [2,3,23]. The quality of such an estimate of the rate depends upon the choice of the dividing surface [2,7]. An attractive feature of this approach is that TST provides an upper bound to the plateau value Γ_{RF} of the standard reactive flux method. This latter quantity is commonly believed to coincide with the true rate, $\Gamma_{\mathrm{RF}}=\Gamma$, such that a variational principle may be used to find the optimal dividing surface and the most accurate estimate of the rate [2]. In the resulting methodology, known as VTST, the dividing surface is varied to find the one which yields the smallest crossing rate, and this rate is then taken to be the best approximation to the true rate constant [2,7,40–42,44,46]. When restricted to planar dividing surfaces, VTST gives for the full rate $\Gamma=\Gamma_f+\Gamma_b$ [42]

$$\Gamma_{\mathrm{VTST}}[\omega]=\Gamma_{\mathrm{TST}}\sqrt{\frac{\beta(\gamma+2\mu)}{2\pi\gamma}}\int_{-\infty}^{\infty}dx\exp\Big[-\beta U(x)$$
$$-\beta\mu\frac{(\mu+\gamma)^2}{\gamma}(x-s)^2\Big], \tag{B3}$$

where Γ_{TST} is defined by Eq. (2.7), and the shift s is determined from the integral equation

$$\int_{-\infty}^{\infty} dx(x-s)\exp\left[-\beta U(x)-\beta\mu\frac{(\mu+\gamma)^2}{\gamma}(x-s)^2\right]=0. \tag{B4}$$

The variational parameter ω [related to μ by Eq. (3.11)] is to be fixed by minimization of $\Gamma_{VTST}[\omega]$. Yet, we have recently proven that the reactive flux rate Γ_{RF} is not a well defined mathematical object [50]. Depending on the dividing surface used, this quantity varies in the interval $0\leqslant\Gamma_{RF}\leqslant\Gamma$, where the upper limit $\Gamma_{RF}=\Gamma$ is achieved only for the perfect dividing surface. As a consequence, the afore-mentioned bounding property of TST, $\Gamma_{VTST}\geqslant\Gamma$, is *not* rigorous and may be violated under some conditions [50,52]. In such cases, VTST will not necessarily yield the most accurate result for the rate, just a variational estimate.

Besides these two variational approaches, there are many other methods in the literature to calculate rate constants in potentials with nonparabolic barriers. Specifically we mention a heuristic method of Calef and Wolynes [37] who suggested that we replace the actual potential by a parabolic barrier with an effective frequency ω_e and use the standard Kramers result, Eq. (2.6) for this parabolic barrier. Dekker [38] applied Rayleigh's quotient, Eq. (B1), to potentials with cusped and parabolic barriers using different (both Kramers' and non-Kramers') approximations for the pertinent eigenfunction. Two straightforward extensions of these Dekker's results to an arbitrary algebraic barrier, Eq. (3.22), have been proposed by Berezhkovskii, Talkner, Emmerich, and Zitserman [47] and Drozdov [25]. Finally, a different method consists in using accurate interpolation techniques to bridge exact solutions of the Kramers problem available in the limits of weak and strong friction [31,48]. However, since none of the above-mentioned methods is variational, we will not consider them here.

[1] H. Kramers, Physica (Utrecht) **7**, 284 (1940).

[2] J. C. Keck, Adv. Chem. Phys. **13**, 85 (1967).

[3] K. J. Laidler, *Theories of Chemical Reaction Rates* (McGraw-Hill, New York, 1969); P. Pechukas, in *Dynamics of Molecular Collisions*, Part B, edited by W. H. Miller (Plenum, New York, 1976), p. 269; Annu. Rev. Phys. Chem. **32**, 159 (1981).

[4] C. Gardiner, *Handbook of Stochastic Methods* (Springer, Berlin, 1983).

[5] H. Risken, *The Fokker–Planck Equation, Methods of Solution and Applications* (Springer, New York, 1989).

[6] J. T. Hynes, in *Theory of Chemical Reaction Dynamics*, edited by M. Baer (CRC, Boca Raton, 1985), Vol. IV, p. 171; A. M. Berezhkovskii, A. N. Drozdov, and V. Yu. Zitserman, Russ. J. Phys. Chem. **62**, 1353 (1988); P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990); V. I. Mel'nikovw, Phys. Rep. **209**, 1 (1991).

[7] S. C. Tucker, in *New Trends in Kramers' Reaction Rate Theory*, edited by P. Talkner and P. Hänggi (Kluwer Academic, Dordrecht, 1995), p. 5; E. Pollak, in *Dynamics of Molecules and Chemical Reactions*, edited by R. E. Wyatt and J. Z. H. Zhang (Dekker, New York, 1996), p. 617.

[8] Chem. Phys. **235**, 1 (1998), special issue on dynamical processes in condensed phases, edited by P. Talkner, E. Pollak, and A. M. Berezhkovskii.

[9] In classical theory of rate constants, the least nonvanishing eigenvalue is often identified with the phenomenological rate constant $\tilde{\Gamma}$ which is the sum of the forward and backward rates, $\tilde{\Gamma}=\tilde{\Gamma}_f+\tilde{\Gamma}_b$, entering a phenomenological linear rate law (see, e.g., Ref. [50]). One must note, however, that there exists a principal difference between these two quantities. The least nonvanishing eigenvalue λ_1 is a well defined mathematical object at all barrier heights including the limiting case of barrierless dynamics. By contrast, the phenomenological rate constant $\tilde{\Gamma}$ allows for an unambiguous definition only for moderate and high barriers, $\beta E\gtrsim 3$, when there is a large gap in the spectrum of the Fokker–Planck operator separating the least nonvanishing eigenvalue from the rest of the spectrum, $\lambda_2/\lambda_1\gtrsim 40$.

[10] R. Lovett, J. Chem. Phys. **84**, 4602 (1986); B. Cartling, *ibid.* **87**, 2638 (1987); A. N. Drozdov and M. Morillo, Phys. Rev. E **54**, 931 (1996).

[11] P. B. Visscher, Phys. Rev. B **14**, 347 (1976); K. Voigtlaender and H. Risken, J. Stat. Phys. **40**, 397 (1985); **41**, 825 (1985); F. Marchesoni, Phys. Rev. B **32**, 1827 (1985); G. J. Moro and A. Polimeno, Chem. Phys. **131**, 281 (1989); A. N. Drozdov and P. Talkner, J. Chem. Phys. **105**, 4117 (1996).

[12] G. J. Moro and A. Polimeno, Chem. Phys. **131**, 281 (1989).

[13] R. Ferrando, R. Spadacini, and G. E. Tommei, Phys. Rev. A **46**, 699 (1992); Phys. Rev. E **48**, 2437 (1993); R. Ferrando, R. Spadacini, G. E. Tommei, and V. I. Mel'nikov, *ibid.* **51**, 1645 (1995).

[14] J. E. Straub, M. Borkovec, and B. J. Berne, J. Chem. Phys. **83**, 3172 (1985); **84**, 1788 (1986); P. Hänggi, T. J. Mroczkowski, F. Moss, and P. V. E. McClintock, Phys. Rev. A **32**, 695 (1985); S. C. Tucker, M. E. Tuckerman, B. J. Berne, and E. Pollak, J. Chem. Phys. **95**, 5809 (1991); J. B. Straus and G. A. Voth, *ibid.* **96**, 5460 (1992); G. K. Schenter, R. P. McRae, and B. C. Garrett, *ibid.* **97**, 9116 (1992); S. Linkwitz, H. Grabert, E. Turlot, D. Esteve, and M. H. Devoret, Phys. Rev. A **45**, 3369 (1992); M. M. Wu, K. Y. R. Billah, and M. Shinozuka, Phys. Rev. E **52**, 3377 (1995); S. K. Reese, S. C. Tucker, and G. K. Schenter, J. Chem. Phys. **102**, 104 (1995); J. S. Bader and B. J. Berne, *ibid.* **102**, 7953 (1995); E. Hershkovitz, Phys. Lett. **108**, 9253 (1998).

[15] A. N. Drozdov, V. Yu. Zitserman, and V. F. Baibuz, Chem. Phys. **88**, 81 (1984); B. Carmeli, V. Mujica, and A. Nitzan, Ber. Bunsenges. Phys. Chem. **95**, 319 (1991); M. Topaler and N. Makri, J. Chem. Phys. **101**, 7500 (1994); A. N. Drozdov, Phys. Lett. A **171**, 175 (1992); Phys. Rev. E **55**, 2496 (1997); A. N. Drozdov and J. J. Brey, Phys. Lett. **237A**, 119 (1998); Phys. Rev. E **57**, 146 (1998); **57**, 1284 (1998).

[16] A. N. Drozdov, J. Chem. Phys. **107**, 3505 (1997); A. N. Drozdov and P. Talkner, *ibid.* **109**, 2080 (1998).

[17] H. C. Brinkman, Physica (Utrecht) **22**, 149 (1956); R. Landauer and J. A. Swanson, Phys. Rev. **121**, 1668 (1961); J. S. Langer, Ann. Phys. (N.Y.) **54**, 258 (1969); B. J. Matkowsky,

Z. Schuss, and E. Ben-Jacob, SIAM (Soc. Ind. Appl. Math.) J. Appl. Math. **42**, 835 (1982).
[18] B. J. Matkowsky and Z. Schuss, SIAM (Soc. Ind. Appl. Math.) J. Appl. Math. **33**, 365 (1977); B. Caroli, C. Caroli, and B. Roulet, J. Stat. Phys. **28**, 757 (1982); D. Ryter, Physica A **130**, 205 (1985); P. Talkner, Z. Phys. B: Condens. Matter **68**, 201 (1987); R. S. Maier and D. L. Stein, J. Stat. Phys. **83**, 291 (1996); Phys. Rev. Lett. **77**, 4860 (1996).
[19] D. Ryter, Physica A **142**, 103 (1987).
[20] A. N. Drozdov, Physica A **187**, 329 (1992).
[21] A. N. Drozdov and J. J. Brey, J. Chem. Phys. **110**, 7133 (1999).
[22] R. F. Grote and J. T. Hynes, J. Chem. Phys. **73**, 2715 (1980); P. Hänggi and F. Mojtabai, Phys. Rev. A **26**, 1168 (1982).
[23] Yu. I. Dakhnovskii and A. A. Ovchinnikov, Phys. Lett. **113A**, 147 (1985); E. Pollak, J. Chem. Phys. **85**, 865 (1986).
[24] H. Grabert, Phys. Rev. Lett. **61**, 1683 (1988); E. Pollak, H. Grabert, and P. Hänggi, J. Chem. Phys. **91**, 4073 (1989); R. Graham, J. Stat. Phys. **60**, 675 (1990).
[25] A. N. Drozdov, Phys. Rev. E **58**, 2865 (1998).
[26] S. R. Larson and M. D. Kostin, J. Chem. Phys. **72**, 1392 (1980).
[27] M. Büttiker, E. P. Harris, and R. Landauer, Phys. Rev. B **28**, 1268 (1983); V. I. Mel'nikov and S. V. Meshkov, J. Chem. Phys. **85**, 1018 (1986); A. N. Drozdov and J. J. Brey, *ibid.* **110**, 2159 (1999).
[28] H. Dekker and A. Maassen van den Brink, Phys. Rev. E **49**, 2559 (1994); A. Maassen van den Brink and H. Dekker, Physica A **237**, 515 (1997).
[29] D. Ryter, J. Stat. Phys. **49**, 751 (1987).
[30] V. I. Mel'nikov, Phys. Rev. E **48**, 3271 (1993).
[31] A. N. Drozdov and S. Hayashi, Phys. Rev. E **60**, 3804 (1999).
[32] D. Borgis and M. Moreau, Mol. Phys. **57**, 33 (1986); E. Pollak and P. Talkner, Phys. Rev. E **51**, 1868 (1995); S. K. Reese and S. C. Tucker, J. Chem. Phys. **105**, 2263 (1996); Chem. Phys. **235**, 171 (1998); A. N. Drozdov and J. J. Brey, *ibid.* **235**, 147 (1998); J. M. Sancho, A. H. Romero, and K. Lindenberg, J. Chem. Phys. **109**, 9888 (1998).
[33] M. M. Klosek, B. J. Matkowsky, and Z. Schuss, Ber. Bunsenges. Phys. Chem. **95**, 331 (1991).
[34] S. H. Northrup and J. T. Hynes, J. Chem. Phys. **69**, 5246 (1978); K. Schulten, Z. Schulten, and A. Szabo, *ibid.* **74**, 4426 (1981); W. Nadler and K. Schulten, *ibid.* **82**, 151 (1985).
[35] N. G. van Kampen, J. Stat. Phys. **17**, 71 (1977); R. S. Larson and M. D. Kostin, J. Chem. Phys. **69**, 4821 (1978); O. Edholm and O. Leimar, Physica A **98**, 313 (1979); W. Bez and P. Talkner, Phys. Lett. **82A**, 313 (1981); F. Marchesoni, Adv. Chem. Phys. **63**, 603 (1985).
[36] A. N. Drozdov and P. Talkner, Phys. Rev. E **54**, 6160 (1996).
[37] D. F. Calef and P. G. Wolynes, J. Phys. Chem. **87**, 3387 (1983).
[38] H. Dekker, Phys. Lett. **112A**, 197 (1985); Physica A **135**, 80 (1986); **136**, 124 (1986).
[39] P. Talkner, Ber. Bunsenges. Phys. Chem. **95**, 327 (1991).
[40] E. Pollak, S. C. Tucker, and B. J. Berne, Phys. Rev. Lett. **65**, 1399 (1990); E. Pollak, J. Chem. Phys. **93**, 1116 (1990); A. M. Frishman, A. M. Berezhkovskii, and E. Pollak, Phys. Rev. E **49**, 1216 (1994).
[41] E. Pollak, J. Phys. Chem. **95**, 10 235 (1991); A. M. Frishman and E. Pollak, J. Chem. Phys. **96**, 8877 (1992).
[42] A. M. Berezhkovskii, E. Pollak, and V. Yu. Zitserman, J. Chem. Phys. **97**, 2422 (1992).
[43] P. Talkner and E. Pollak, Phys. Rev. E **47**, 21 (1993).
[44] E. Pollak and P. Talkner, Phys. Rev. E **47**, 922 (1993); P. Talkner and E. Pollak, *ibid.* **50**, 2646 (1994).
[45] P. Talkner, Chem. Phys. **180**, 199 (1994).
[46] A. Starobinets, I. Rips, and E. Pollak, J. Chem. Phys. **104**, 6547 (1996).
[47] A. M. Berezhkovskii, P. Talkner, J. Emmerich, and V. Yu. Zitserman, J. Chem. Phys. **105**, 10 890 (1996).
[48] A. N. Drozdov, J. Chem. Phys. **111**, 6481 (1999).
[49] R. Zwanzig, J. Stat. Phys. **9**, 215 (1973).
[50] A. N. Drozdov and S. C. Tucker, Phys. Rev. E **61**, 2457 (2000).
[51] The situation is slightly different in the limit of vanishing friction, $\gamma \to 0$, in which case the denominators D_k and thus the rate functionals Γ_k [see Eq. (4.2)] may become negative as ω goes to zero. Note, however, that away from the limit $\omega \ll \Omega$ such that the denominators D_k are positive, both rate functionals $\Gamma_1[\omega]$ and $\Gamma_2[\omega]$ have global minima which approach the TST result (2.7) as $\gamma \to 0$.
[52] A. N. Drozdov and S. C. Tucker, J. Chem. Phys. **112**, 5251 (2000).