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Optimal barrier subdivision for Kramers' escape rate

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Abstract. We examine the effect of subdividing the potential barrier along the reaction coordinate on Kramers' escape rate for a model potential. Using the known supersymmetric potential approach, we show the existence of an optimal number of subdivisions that maximizes the rate.

Keywords. Kramers problem; activated processes; reaction rates.

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1. Introduction

The problem of surmounting a potential or, more generally, a free energy barrier is a classical one that appears in all processes having thermally activated kinetics. This problem was originally addressed by Kramers in the context of a bistable potential energy curve [1]. He provided an approximate solution for the rate of escape over the barrier in a high barrier low noise limit. In the commonly encountered high friction limit, the bistable potential is usually parameterized in terms of the height of the barrier at the potential maximum and the width of, or the distance under the barrier connecting the initial and the final states (potential minima). Since Kramers' original work, there has been a number of refinements as well as varied novel applications of his solution, and a large volume of literature exists on this [2, 3].

There are, however, situations where the initial and the final states are separated by a barrier which is so high that the estimated reaction rate is very small, and yet the reaction actually turns out to proceed at a substantially higher rate. The enhancement is attributed to the catalytic action, notably of an enzyme in a biochemical reaction that forms a 'transition state' complex with the substrate giving a reduced barrier height [4]. We, however, envisage here an alternative scenario where the enzyme effectively reduces the activation energy by subdividing the reaction path into a number of discrete steps each requiring a much smaller barrier crossing. These subdivisions are expected to correspond to the discrete conformational/configurational changes of the macromolecules, proteins say. Besides looking for a physical consequence of the barrier subdivision, in its own right, the problem can be viewed as an exercise on rate processes in dissipative systems. In the present work we have considered the effect of the barrier

subdivision on the reaction rate in the high friction limit. This we have done for a W-shaped model potential barrier whose subdivision can be well parameterized. Our analysis of the problem is based on the supersymmetric potential technique [5–7].

2. The methodology

It is sufficient for our purpose to note that in the high friction limit, Kramers' escape problem is one of solving the Smoluchowski equation (SE):

$$\frac{\partial}{\partial t}P(x,t) = D\frac{\partial}{\partial x}\left(\frac{\partial}{\partial x} + \beta U'(x)\right)P(x,t), \tag{1}$$

where $P(x,t)$ is the probability density associated with the particle position, $U'(x) = \mathrm{d}U/\mathrm{d}x$ with $U(x)$ being the 'double well'-potential, D the diffusion constant and $\beta = (kT)^{-1}$ is the inverse temperature. With the ansatz

$$P(x,t) = \phi(x)\mathrm{e}^{-\beta U(x)/2}\mathrm{e}^{-\lambda t}, \tag{2}$$

the SE is converted to an Euclidean Schrödinger equation for ϕ:

$$H_+\phi_+ = E_+\phi_+ \tag{3}$$

with $H_+ = A^+A$ being positive semi-definite, where $E_+ = \lambda/D$ and

$$A = \frac{\partial}{\partial x} + \frac{1}{2}\beta U'(x), \tag{4}$$

$$A^+ = -\frac{\partial}{\partial x} + \frac{1}{2}\beta U'(x). \tag{5}$$

This Hamiltonian H_+ corresponds to the motion of a particle in the potential

$$V_+(x) = \left(\frac{1}{2}\beta U'(x)\right)^2 - \frac{1}{2}\beta U''(x). \tag{6}$$

For a high barrier, the escape rate is determined by the smallest nonzero eigenvalue, $\lambda_1 = DE_+^1$, of the SE where E_+^1 is the eigenvalue of the first excited state of eq. (3). On the other hand, this eigenstate is degenerate with the ground state ϕ_-^0 of the 'supersymmetric partner potential' $V_-(x)$ given by

$$V_-(x) = \left(\frac{1}{2}\beta U'(x)\right)^2 + \frac{1}{2}\beta U''(x) \tag{7}$$

so that $H_-\phi_-^0 = E_-\phi_-^0$ with $H_- = AA^+$ and $E_- = E_+^1$. The problem thus boils down to finding the ground state eigenvalue of this 'partner' potential.

3. The model and its solution

3.1 *The model potential and parameterization of subdivision*

For simplicity we consider a symmetric W-potential. For a full characterization of this potential we require two parameters, namely, the height U_0 and the width under the

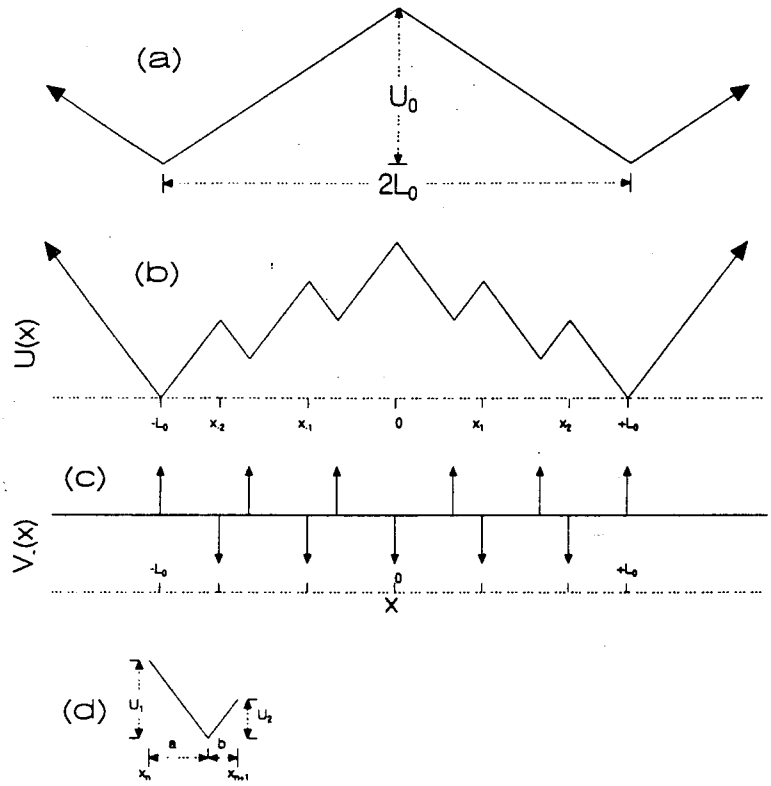

Figure 1. (**a**) The model potential. (**b**) Plot of the subdivided model potential: $U(x)$ versus x, when $N = 3$. Note the change in the slope of the left- and right-confining walls from that of (**a**). (**c**) Plot of $V_-(x)$ versus x (not to scale). (**d**) A figure showing a step of the subdivided potential found between the intervals x_n and x_{n+1}.

potential $2L_0$ (see figure 1a). We now subdivide the barrier between the initial and final states into a series of smaller connecting barriers of many steps (see figure 1b). In order to examine the effect of barrier subdivision on the reaction rate systematically, it is necessary to parameterize the subdivision in a physically, reasonable manner. Consider the step located between x_n and x_{n+1} (figure 1d). We choose U_1, U_2 and the associated widths a, b (shown in the figure) such that $U_1/a = U_2/b$. This choice simplifies the calculation further. Note that $x_{n+1} - x_n = a + b$. If we have a total of N such equally spaced steps from the top of the barrier on either side, then $L_0 = Na + (N-1)b$, while $U_0 = NU_1 - (N-1)U_2$. We introduce a parameter ρ defined as

$$\rho \equiv \frac{(N-1)U_2}{NU_1} = \frac{(N-1)b}{Na}. \tag{8}$$

The aim is, given U_0 and L_0, to find the escape rate for different values of barrier subdivision consistent with the high barrier limit, i.e. for various values of N. Such parameterization is physically reasonable as it not only keeps the barrier height and its width fixed, it also keeps the area under the barrier approximately constant as N is

varied. Introducing a dimensionless potential $u(x)=\frac{1}{2}\beta U(x)$, the 'supersymmetric partner potential' to $V_+(x)$, namely, $V_-(x)$, is given by

$$V_-(x)=(u'(x))^2+u''(x) \tag{9}$$

which for the considered potential takes the form

$$V_-(x)=\left(\frac{u_1}{a}\right)^2-\left(\frac{2u_1}{a}\right)\sum_{n=-N}^{+N}[\delta(x-x_n)-\delta(x-x_n-a)], \tag{10}$$

where $u_1=\frac{1}{2}\beta U_1$. Note that the potential $V_-(x)$ is a series of attractive and repulsive delta-potentials superimposed over a constant potential (see figure 1c). Changing the variable x to $y=x/Na$ leads to a new Hamiltonian h_- given by

$$h_-\equiv a_0^2H_-=-\frac{\partial^2}{\partial y^2}+(u_1^0)^2-2u_1^0\sum_{n=-N}^{+N}[\delta(y-y_n)-\delta(y-y_n-a_1)], \tag{11}$$

where $a_0=Na$, $u_1^0=Nu_1$, $a_1=1/N$, $b_1=\rho/(N-1)$ and $y_n=n(a_1+b_1)$. With this, $h_-\phi_-^0(y)=e_-\phi_-^0(y)$, where e_- is a dimensionless quantity equal to $a_0^2E_-$.

3.2 *Solution*

We use transfer matrix method to find the ground state energy. The ground state wave function ϕ_-^0 is of the form $Ae^{-ky}+Be^{ky}$ peaked around the positions of the delta potentials. Consider one period of the potential, say, the interval between y_n and y_{n+1}. Assume the wave function of the form

$$\phi_1(y)=A_ne^{-k(y-y_n)}+B_ne^{k(y-y_n)}, \tag{12}$$

for the interval $y_{n-1}+a_1\leqslant y\leqslant y_n$ and the wave function of the form

$$\phi_2(y)=C_ne^{-k(y-y_n-a_1)}+D_ne^{k(y-y_n-a_1)} \tag{13}$$

for the interval $y_n\leqslant y\leqslant y_n+a_1$ with $k=[(u_1^0)^2-e_-]^{1/2}$. By matching the wave function at y_n, i.e. $\phi_1(y_n)=\phi_2(y_n)$, and the integrating eq. (11) around y_n noting that there is a negative delta-potential of strength $2u_1^0$, i.e. $\phi_1'(y_n)-\phi_2'(y_n)-2u_1^0\phi_1(y_n)=0$, we get

$$\begin{pmatrix}C_n\\D_n\end{pmatrix}=\begin{pmatrix}(1+\alpha)e^{-ka_1} & \alpha e^{-ka_1}\\ -\alpha e^{ka_1} & (1-\alpha)e^{ka_1}\end{pmatrix}\begin{pmatrix}A_n\\B_n\end{pmatrix}=\mathbf{T}_1\begin{pmatrix}A_n\\B_n\end{pmatrix} \tag{14}$$

relating the two pairs of amplitudes ($\alpha=u_1^0/k$). Next, matching the wave function having amplitudes C_n and D_n with the wave function having amplitudes A_{n+1} and B_{n+1} (found in the interval $y_n+a_1\leqslant y\leqslant y_{n+1}$) and integrating eq. (11) around y_n+a_1 noting that a positive delta-potential of strength $2u_1^0$ is located there, we get

$$\begin{pmatrix}A_{n+1}\\B_{n+1}\end{pmatrix}=\begin{pmatrix}(1-\alpha)e^{-kb_1} & -\alpha e^{-kb_1}\\ \alpha e^{kb_1} & (1+\alpha)e^{kb_1}\end{pmatrix}\begin{pmatrix}C_n\\D_n\end{pmatrix}=\mathbf{T}_2\begin{pmatrix}C_n\\D_n\end{pmatrix}. \tag{15}$$

The transfer matrix, $\mathbf{T}$, relating the amplitudes A_{n+1}, B_{n+1} to the amplitudes A_n and B_n,

$$\begin{pmatrix}A_{n+1}\\B_{n+1}\end{pmatrix}=\mathbf{T}\begin{pmatrix}A_n\\B_n\end{pmatrix} \tag{16}$$

will then be a product of the matrices $\mathbf{T}_1$ and $\mathbf{T}_2$, i.e., $\mathbf{T} = \mathbf{T}_2\mathbf{T}_1$. The amplitudes just before the end of the N-th step A_N, B_N are related to the amplitudes A_0, B_0 at the top left side of the barrier by a product of N of these transfer matrices

$$\begin{pmatrix} A_N \\ B_N \end{pmatrix} = \mathbf{T}^N \begin{pmatrix} A_0 \\ B_0 \end{pmatrix}. \tag{17}$$

Symmetry of the potential about $y = 0$ implies that the ground state wave function is symmetric, i.e., $\phi^0_-(-y) = \phi^0_-(y)$. Using matching and integration at and around the origin where there is a negative delta-potential with the symmetry property of the wave function relates A_0 and B_0,

$$B_0 = \frac{1+\alpha}{1-\alpha} A_0. \tag{18}$$

Since we are concerned with a bound state solution, $B_N = 0$. Using this and eq. (18) in eq. (17) enables us to get

$$(1-\alpha)(\mathbf{T}^N)_{21} + (1+\alpha)(\mathbf{T}^N)_{22} = 0, \tag{19}$$

the *lowest positive* solution of which gives us the value of e_- when u_0, ρ and N are specified. The expressions for the matrix elements $(\mathbf{T}^N)_{21}$ and $(\mathbf{T}^N)_{22}$ are given in the Appendix.

4. Results and discussion

Now we consider the solution of eq. (19). The result could be better appreciated if we compare it with the corresponding escape rate for the original W-potential with no barrier subdivision (figure 1a). Applying the same technique as above, the equation corresponding to eq. (19) to be solved is

$$\alpha_0 + (1-\alpha_0)e^{2k_0} = 0, \tag{20}$$

where $\alpha_0 = u_0/k_0$, $k_0 = [u_0^2 - e^0_-]^{1/2}$ with $u_0 = \frac{1}{2}\beta U_0$. In this case, $e^0_- = L_0^2 E^0_-$. The inverse of DE^0_- is the time required to go from one minimum to the other in figure(1a) and we define the corresponding escape rate as DE^0_- for the original 'W' potential. Then the ratio, f_N, of the escape rate, DE_-, over the potential with a certain barrier subdivision to that of escape rate, DE^0_-, over the original W-potential is given by

$$f_N \equiv \frac{E_-}{E^0_-} = (1+\rho)^2 \frac{e_-}{e^0_-}. \tag{21}$$

We call this ratio, f_N, as the *enhancement factor*. It may be worthwhile pointing out here that we have used the first passage time from one minimum to the other in the original potential as a scale factor. This is because the subdivided potential is rugged on the 'down hill part' as well, which could give rise to a considerably different transit time compared to the situation if only 'sliding down' on a smooth line were allowed.

There are only two parameters in our model, namely u_0, which is the total barrier height and ρ, which essentially represents the steepness of the local barriers. We chose u_0 (so as to be in the high barrier limit) holding ρ fixed and explored the enhancement

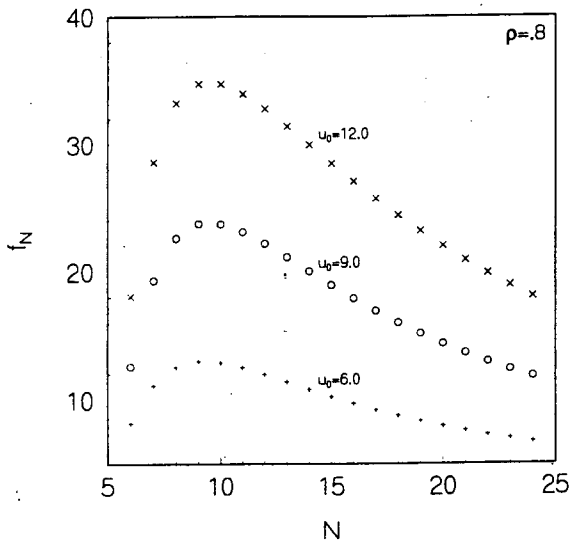

Figure 2. Plots of f_N versus N for three different values of u_0 (i.e. 6·0, 9·0, 12·0) with fixed $\rho(=0{\cdot}8)$. Note that all the optimal values occur at $N=9$.

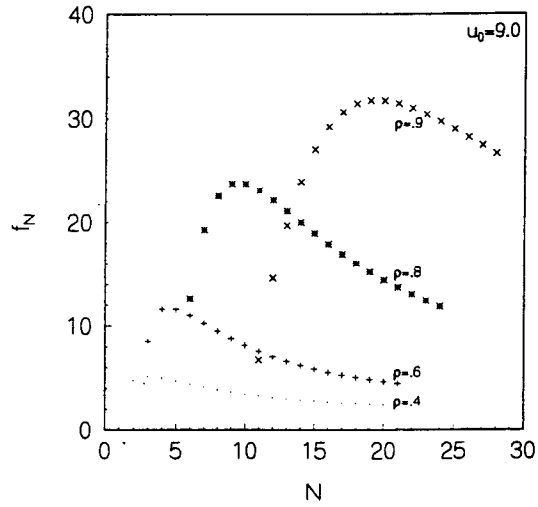

Figure 3. Plots of f_N versus N for four different values of ρ (i.e. 0·4, 0·6, 0·8, 0·9) with fixed $u_0(=9{\cdot}0)$.

factor, f_N, for various values of barrier subdivision, N. Figure 2 shows plots of f_N versus N for three different choices of u_0 with fixed $\rho\ (=0{\cdot}8)$. For this case, the enhancement factor at the optimal barrier subdivision, N_{op}, increases as u_0 is increased reaching a value as high as 35 for $u_0 = 12{\cdot}0$, while N_{op} remains constant (here 9) suggesting that

the steepness of the local barrier determines N_{op}. In figure 3, we have varied ρ for a fixed value of $u_0 (= 9{\cdot}0)$. In this case, both N_{op} and the enhancement factor increase as ρ is increased. (Note that in both the figures N starts at values larger than 2 for higher values of ρ. This is due to the fact that for these values of ρ, the enhancement factor is less than unity for low values of N and correspond to the situation where $U_2 > U_1$.)

We have verified that these trends are general. Thus, there is an optimal value of barrier subdivision, N_{op}, at which the escape rate takes a maximum value. The existence of N_{op} may be readily understood by a reference to the potential $V_-(x)$. The binding energy of this localized ground state of the individual negative energy delta-functions and its lowering due to mutual overlap of the neighbouring bound states (banding effect) are oppositely affected by N.

It may be worthwhile to mention here that in addition to changing the terrain (say steepness) of the intermediate barrier (connecting the initial and final states) by the subdivision, the outer barriers were also made to change their steepness accordingly for the sake of simplicity (see figures 1a and 1b). Because of this increased steepness, they become more confining than with their original slope and, thus, give rise to an overestimation of the enhancement factor. We have verified this by retaining the original slope of the outer barriers. However, the main features remain the same. On the other hand, due to the monotonic increase of the optimal enhancement factor with the barrier height, its value could be much larger than the ones considered here for barrier heights that exist in chemical and physical processes.

We remark that this problem can be viewed, approximately, as that of finding the mean first passage time of a biased random walk [8]. However, this would imply assigning values to the forward and the backward transition rates for the individual sub-barriers taken in isolation as input, i.e. assuming that the potentials to the left and right sides of each sub-barrier are totally confining, and then using these input values to calculate the global escape rate for the coupled sub-barriers. We have found that while this gives an optimal barrier subdivision for the escape rate consistent with the present result, the enhancement factor is considerably over-estimated by this random walk approach. The present SUSY-based calculation goes beyond this uncontrolled approximation.

It would be interesting to examine and optimize the effect of an athermal (possibly colored) noise (the 'blow torch' of Landauer [9, 10]) on one of the steps of our subdivided potential curve. This is under investigation.

In conclusion, we have shown that the Kramers' rate for the escape over a given potential barrier, in the high barrier high friction limit, can be substantially enhanced by subdividing the barrier optimally. This might provide an alternative scenario for certain activated processes where the measured escape rate is substantially higher than that anticipated.

Appendix A

To find the elements of the matrix $\mathbf{T}^N$ we decompose the transfer matrix $\mathbf{T}$ as a product of three matrices, i.e.

$$\mathbf{T} = \mathbf{R}\Lambda\mathbf{L} \tag{A1}$$

so that Λ is a diagonal matrix whose diagonal elements are the eigenvalues of **T**. The matrices **L** and **R** are, respectively, made up of the left- and right-eigenvectors of **T** such that $\mathbf{LR} = \mathbf{RL} = \mathbf{I}$. With this decomposition,

$$\mathbf{T}^N = \mathbf{R}\Lambda^N\mathbf{L} \tag{A2}$$

whose two elements of our interest, $(\mathbf{T}^N)_{21}$ and $(\mathbf{T}^N)_{22}$ are expressed as

$$(\mathbf{T}^N)_{21} = \frac{T_{21}(-\lambda_-^N + \lambda_+^N)}{Q} \tag{A3}$$

and

$$(\mathbf{T}^N)_{22} = \frac{(T_{11} - T_{22})(\lambda_-^N - \lambda_+^N) + (\lambda_-^N + \lambda_+^N)Q}{2Q}. \tag{A4}$$

$\lambda_\pm$ are the eigenvalues of **T** given by

$$\lambda_\pm = \frac{1}{2}(T_{11} + T_{22} \pm Q) \tag{A5}$$

with T_{ij} as the matrix elements of **T** and $Q = [(T_{11} - T_{22})^2 + 4T_{12}T_{21}]^{1/2}$.

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