KRAMERS TURNOVER THEORY FOR A TRIPLE WELL POTENTIAL*

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Kramers turnover theory is solved for a particle in a symmetric triple well potential for temperatures above the crossover temperature between tunneling and activated barrier crossing. Comparison with the turnover theory for a double well potential shows that the presence of the intermediate well always leads to a decrease of the reaction rate. At most though, the rate is a factor of two smaller than in the case of a double well potential.

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1. Introduction

Sixty years ago Kramers [1] considered the problem of the rate of escape of a thermal particle, interacting with a heat bath, trapped in a potential well, separated from a different well by a barrier of height $V^{\ddagger}$. When the damping strength γ was sufficiently small, Kramers showed that the rate increases linearly with γ. In the limit of strong friction, the rate was found to decrease as $1/\gamma$. The rate as a function of the damping strength was thus predicted to be a bell shaped function. Finding this bell shaped function for all values of the damping is known as the Kramers turnover problem, since it was posed by Kramers but he did not present a solution.

The full solution of the turnover problem in the presence of a single, double or periodic potential well was found through the seminal works of Mel'nikov and Meshkov (MM) [2, 3] and Pollak, Grabert and Hänggi

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(PGH) [4] during the late 1980's. Mel'nikov and Meshkov found a solution in the presence of Ohmic friction for the underdamped to the moderate friction regime. PGH generalized MM's result for arbitrary friction strength as well as for memory friction. These works also led to a semiclassical solution for the rate [5], valid provided that the temperature was not lower than the crossover temperature between tunneling dominated escape and activated escape. Extension of PGH theory to temperatures below the crossover temperature may be found in Ref. [6]. Extension of PGH theory to motion on a periodic potential may be found in Refs. [7–9]. Moro and Polimeno [10] extended the MM approach to a problem of an angular potential with four symmetric wells, modeling the trans-gauche isomerization of n-butane.

Recent investigations of electron transfer on molecular bridges [11–14] have raised interest in solution of the Kramers turnover problem for a system in which two deep wells are connected by a series of N shallow wells [15]. In this paper, we present a solution of the turnover problem for the case of two symmetric deep wells connected through a single shallow well. We find that in the underdamped region, the escape rate out of the left well may be *increased* by up to 40% relative to the escape rate in a symmetric double well potential. However, the net rate from the left well into the right well is always reduced relative to the double well potential case. This reduction becomes maximal in the spatial diffusion limited regime, where the reduction is by a factor of two.

In Section 2 we present the solution of the turnover problem for the three well system and apply it to a model system. We end in Section 3 with a Discussion.

2. Turnover theory for a triple well potential

2.1. Preliminaries

The classical equation of motion governing the dynamics of a particle with unit mass and coordinate q is the Generalized Langevin Equation (GLE)

$$\ddot{q} + \frac{dw(q)}{dq} + \int^{t} dt' \gamma(t-t')\dot{q}(t') = \xi(t)\,, \tag{2.1}$$

where $w(q)$ is the triple well potential whose shape is shown schematically in Fig. 1, $\gamma(t)$ is the time dependent friction function, the Gaussian random force $\xi(t)$ has zero mean and is related to the friction function through the fluctuation dissipation relation at temperature T, $\langle \xi(t)\xi(t')\rangle = k_{\mathrm{B}}T\gamma(t-t')$. The quantum version of the dynamics would involve replacing the coordinate and momentum of the particle by the respective operators and the

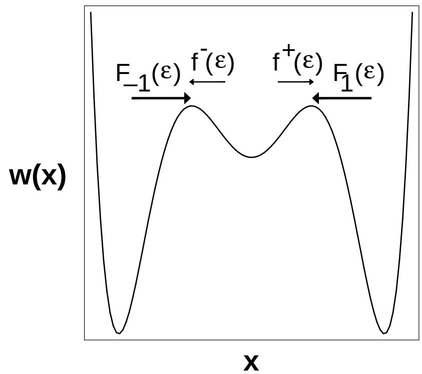

Fig. 1. Symmetric triple well potential. The arrows indicate the probability fluxes at the barriers out of the deep wells (thick arrows) and out of the shallow well (thin arrows).

fluctuating force by another operator whose symmetrized correlation function satisfies the quantum mechanical fluctuation dissipation relation, as described for example in Ref. [16]. In the symmetric triple well problem one can consider two different rates, the rate of escape from the deep well and from the middle shallow well. As shown by PGH, any of these rates will be factorizable into three different terms. The first is the Transition State Theory (TST) rate:

$$\Gamma_{\mathrm{TST}_i} = \frac{\omega_i}{2\pi} \mathrm{e}^{-\beta V_i^{\ddagger}} , \tag{2.2}$$

where ω_i is the frequency in the i-th well and $V_i^{\ddagger}$ is the barrier height for escape from the i-th well. For the middle well ($i = 0$), the TST rate should be multiplied by a factor of 2 since escape occurs to the left and right deep wells, as follows from the steady state equations (see Eqs. (2.7)–(2.10) and Eq. (2.14) below).

The second term is the spatial diffusion factor. Since we are dealing with a symmetric potential, the parabolic barrier frequencies ($\omega^{\ddagger}$) of both barriers are identical. Using the 'hat' notation for the Laplace transform:

$$\hat{\gamma}(s) = \int_0^{\infty} dt \mathrm{e}^{-st} \gamma(t) \tag{2.3}$$

and letting $\tilde{\omega}_n = \frac{2\pi n}{\hbar\beta}$ denote the Matsubara frequencies, the spatial diffusion factor in the parabolic barrier limit is [17]:

$$\Xi_i = \frac{\lambda^{\ddagger}}{\omega^{\ddagger}} \prod_{n=1}^{\infty} \frac{\omega_i^2 + \tilde{\omega}_n^2 + \tilde{\omega}_n \hat{\gamma}(\tilde{\omega}_n)}{-\omega^{\ddagger 2} + \tilde{\omega}_n^2 + \tilde{\omega}_n \hat{\gamma}(\tilde{\omega}_n)} . \tag{2.4}$$

The unstable mode parabolic barrier frequency $\lambda^\ddagger$ is the positive solution of the Kramers–Grote–Hynes equation

$$\lambda^{\ddagger^2} + \lambda^\ddagger \hat{\gamma}(\lambda^\ddagger) = \omega^{\ddagger^2} . \tag{2.5}$$

The third term is the 'depopulation factor' for the i-th well Υ_i so that the overall rate from the i-th well is given by the expression

$$\Gamma_i = \Gamma_{\mathrm{TST}_i} \Upsilon_i \Xi_i . \tag{2.6}$$

The central purpose of this paper is to provide an expression for the depopulation factors for the triple well system.

2.2. The triple well depopulation factors

As shown in Fig. 1, there are four fluxes to be considered. $F_{-1}(\varepsilon)$ ($F_1(\varepsilon)$) is the flux of particles approaching the left (right) barrier from the left (right) well, at the (reduced) energy $\varepsilon = \frac{E}{k_{\mathrm{B}}T}$, and we take the zero of energy to be at the barrier tops. $f^+(\varepsilon)$ ($f^-(\varepsilon)$) is the flux of particles approaching the right (left) barrier from the middle well. There are also two energy transfer kernels that play a role in the dynamics. $P_{-1}(\varepsilon|\varepsilon')$ ($P_1(\varepsilon|\varepsilon')$) is the probability that the particle leaving the left (right) barrier with energy ε' towards the left (right), returns to the barrier with energy ε. By symmetry $P_{-1}(\varepsilon|\varepsilon') = P_1(\varepsilon|\varepsilon')$ so we need only to refer to one of them, which we denote as P. The second kernel $p(\varepsilon|\varepsilon')$ is the conditional probability that a particle leaving the left (right) barrier with energy ε', reaches the right (left) barrier with energy ε.

We assume that a particle hitting a barrier at energy ε is transmitted with probability $T(\varepsilon)$ or reflected with the probability $R(\varepsilon) = 1 - T(\varepsilon)$. We are now in a position to write down the following steady state equations for the fluxes:

$$F_{-1}(\varepsilon) = \int_{-\infty}^{\infty} d\varepsilon' P(\varepsilon|\varepsilon') \big(R(\varepsilon')F_{-1}(\varepsilon') + T(\varepsilon')f^-(\varepsilon')\big) , \tag{2.7}$$

$$f^-(\varepsilon) = \int_{-\infty}^{\infty} d\varepsilon' p(\varepsilon|\varepsilon') \big(R(\varepsilon')f^+(\varepsilon') + T(\varepsilon')F_1(\varepsilon')\big) , \tag{2.8}$$

$$f^+(\varepsilon) = \int_{-\infty}^{\infty} d\varepsilon' p(\varepsilon|\varepsilon') \big(R(\varepsilon')f^-(\varepsilon') + T(\varepsilon')F_{-1}(\varepsilon')\big) , \tag{2.9}$$

$$F_1(\varepsilon) = \int_{-\infty}^{\infty} d\varepsilon' P(\varepsilon|\varepsilon') \big(R(\varepsilon')F_1(\varepsilon') + T(\varepsilon')f^+(\varepsilon')\big) . \tag{2.10}$$

To solve these equations one must define the boundary conditions for the various fluxes, this will be done below. Here we sketch how these equations may be solved. Following the appendix of Ref. [5] we define two sided Laplace transforms as:

$$N_i(s) = \int_{-\infty}^{\infty} d\varepsilon \mathrm{e}^{-s\varepsilon} R(\varepsilon) F_i(\varepsilon) \tag{2.11}$$

and similarly for the middle well fluxes, we define $n^-(s)$ and $n^+(s)$. The two sided Laplace transforms of the energy transfer kernels are denoted as:

$$\tilde{P}(s) = \int_{-\infty}^{\infty} d\varepsilon \mathrm{e}^{-s(\varepsilon-\varepsilon')} P(\varepsilon|\varepsilon') \,. \tag{2.12}$$

We also assume that the transmission probability is that of the parabolic barrier, that is:

$$T(\varepsilon) = \frac{\mathrm{e}^{\alpha\varepsilon}}{1+\mathrm{e}^{\alpha\varepsilon}} \,, \tag{2.13}$$

where $\alpha = \frac{2\pi}{\hbar\beta\lambda^{\ddagger}}$.

With these notations and some algebra, one may reduce the four steady state equations (2.7)–(2.10) to two equations:

$$\begin{aligned} N(s-\alpha) &\equiv N_{-1}(s-\alpha) - n^-(s-\alpha) + N_1(s-\alpha) - n^+(s-\alpha) \\ &= \frac{(1-\tilde{P}(s))(1-\tilde{p}(s))}{\tilde{P}(s)\tilde{p}(s)-1} N(s) \,, \end{aligned} \tag{2.14}$$

$$\begin{aligned} \mathit{\Delta} N(s-\alpha) &\equiv N_{-1}(s-\alpha) - n^-(s-\alpha) - N_1(s-\alpha) + n^+(s-\alpha) \\ &= -\frac{(1-\tilde{P}(s))(1+\tilde{p}(s))}{\tilde{P}(s)\tilde{p}(s)+1} \mathit{\Delta} N(s) \,. \end{aligned} \tag{2.15}$$

These equations may be now solved as detailed in the Appendix of Ref. [5], the only elements missing are the boundary conditions.

We distinguish between two situations. One, the particle is initiated thermally into the left well, such that $F_{-1}(\varepsilon) \sim \mathrm{e}^{-\varepsilon}$ for energies that are sufficiently below the barrier, while all other populations are zero. The net rate out of the left well is then:

$$\mathit{\Gamma}_{-1} = \int_{-\infty}^{\infty} d\varepsilon T(\varepsilon) \left(F_{-1}(\varepsilon) - f^-(\varepsilon)\right) = \tfrac{1}{2}\left(N(-\alpha) + \mathit{\Delta} N(-\alpha)\right) \,. \tag{2.16}$$

This rate may be further subdivided as the exit rate into the middle well and into the right well. The former is:

$$\Gamma_{0\leftarrow -1} = N(-\alpha) \tag{2.17}$$

and the latter is

$$\Gamma_{1\leftarrow -1} = \tfrac{1}{2}\left(-N(-\alpha) + \Delta N(-\alpha)\right) . \tag{2.18}$$

One now finds that the depopulation factor for the total rate out of the left well is given by the expression:

$$\Upsilon_{-1} = \frac{1}{2}\left(\exp\left(\frac{\hbar\beta\lambda^{\ddagger}\sin(\hbar\beta\lambda^{\ddagger}/2)}{2\pi}\int\limits_{-\infty}^{\infty} d\tau \frac{\ln\frac{(\tilde{P}(-i(\tau+\frac{1}{2}))-1)(\tilde{p}(-i(\tau+\frac{1}{2}))-1)}{1-\tilde{P}(-i(\tau+\frac{1}{2}))\tilde{p}(-i(\tau+\frac{1}{2}))}}{\cosh(\tau\hbar\beta\lambda^{\ddagger}) - \cos(\hbar\beta\lambda^{\ddagger}/2)}\right)\right.$$
$$\left. + \exp\left(\frac{\hbar\beta\lambda^{\ddagger}\sin(\hbar\beta\lambda^{\ddagger}/2)}{2\pi}\int\limits_{-\infty}^{\infty} d\tau \frac{\ln\frac{(1-\tilde{P}(-i(\tau+\frac{1}{2})))(\tilde{p}(-i(\tau+\frac{1}{2}))+1)}{1+\tilde{P}(-i(\tau+\frac{1}{2}))\tilde{p}(-i(\tau+\frac{1}{2}))}}{\cosh(\tau\hbar\beta\lambda^{\ddagger}) - \cos(\hbar\beta\lambda^{\ddagger}/2)}\right)\right) . \tag{2.19}$$

Similarly, the depopulation factor for the partial rate into the middle well is:

$$\Upsilon_{0\leftarrow -1} = \exp\left(\frac{\hbar\beta\lambda^{\ddagger}\sin(\hbar\beta\lambda^{\ddagger}/2)}{2\pi}\int\limits_{-\infty}^{\infty} d\tau \frac{\ln\frac{(\tilde{P}(-i(\tau+\frac{1}{2}))-1)(\tilde{p}(-i(\tau+\frac{1}{2}))-1)}{1-\tilde{P}(-i(\tau+\frac{1}{2}))\tilde{p}(-i(\tau+\frac{1}{2}))}}{\cosh(\tau\hbar\beta\lambda^{\ddagger}) - \cos(\hbar\beta\lambda^{\ddagger}/2)}\right) . \tag{2.20}$$

Finally the depopulation factor for the partial rate into the right well is:

$$\Upsilon_{1\leftarrow -1} = \frac{1}{2}\left(-\exp\left(\frac{\hbar\beta\lambda^{\ddagger}\sin(\hbar\beta\lambda^{\ddagger}/2)}{2\pi}\int\limits_{-\infty}^{\infty} d\tau \frac{\ln\frac{(\tilde{P}(-i(\tau+\frac{1}{2}))-1)(\tilde{p}(-i(\tau+\frac{1}{2}))-1)}{1-\tilde{P}(-i(\tau+\frac{1}{2}))\tilde{p}(-i(\tau+\frac{1}{2}))}}{\cosh(\tau\hbar\beta\lambda^{\ddagger}) - \cos(\hbar\beta\lambda^{\ddagger}/2)}\right)\right.$$
$$\left. + \exp\left(\frac{\hbar\beta\lambda^{\ddagger}\sin(\hbar\beta\lambda^{\ddagger}/2)}{2\pi}\int\limits_{-\infty}^{\infty} d\tau \frac{\ln\frac{(1-\tilde{P}(-i(\tau+\frac{1}{2})))(\tilde{p}(-i(\tau+\frac{1}{2}))+1)}{1+\tilde{P}(-i(\tau+\frac{1}{2}))\tilde{p}(-i(\tau+\frac{1}{2}))}}{\cosh(\tau\hbar\beta\lambda^{\ddagger}) - \cos(\hbar\beta\lambda^{\ddagger}/2)}\right)\right) . \tag{2.21}$$

The second possibility is that the particle is initiated in the middle well such that $f^{+,-} \sim \mathrm{e}^{-\varepsilon}$. The net rate out of the middle well is:

$$\Gamma_0 = -N(-\alpha) \tag{2.22}$$

and the depopulation factor is identical to the one given in Eq. (2.20).

To complete the solution for the turnover theory, one must specify the probability kernels. In the quantum limit, these are not Gaussian, however, as shown in Refs. [16,18] use of a Gaussian kernel leads to only small errors. We will restrict ourselves to the Gaussian kernels, whose two sided Laplace transforms have the form:

$$\tilde{P}(s) = \mathrm{e}^{-\Delta(s^2+\frac{1}{4})}, \quad (2.23)$$

$$\tilde{p}(s) = \mathrm{e}^{-\delta(s^2+\frac{1}{4})}, \quad (2.24)$$

where Δ is the (reduced) energy loss of the particle as it traverses for one period over the big well at 0 energy, and δ is the energy loss of the particle as it traverses from the left barrier to the right barrier over the middle well.

2.3. A numerical example

The depopulation factors of the symmetric triple well system depend on three dimensionless parameters $\alpha = \hbar\beta\lambda^{\ddagger}$, δ and Δ. In the semiclassical theory used here, the effective action quantum α is restricted to values between zero and 2π where $\alpha = 0$ describes the classical limit. The temperature corresponding to $\alpha = 2\pi$ is known as the crossover temperature below which tunneling dominates the transitions between states of local potential energy minima [16].

Panel (a) of Fig. 2 shows the total depopulation factor Υ_{-1} in the classical limit, *i.e.* for $\alpha = 0$ as a function of the energy loss δ in the smaller well and of the ratio of energy losses Δ/δ. The depopulation factor is a monotonically increasing function of both variables δ and Δ/δ. It approaches unity when either argument goes to infinity. Panel (b) shows how the depopulation

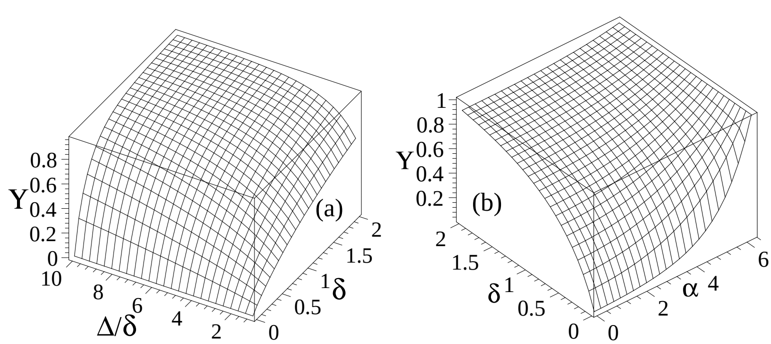

Fig. 2. In panel (a) the depopulation factor Υ_{-1} is displayed in the classical limit as a function of the energy loss δ in the middle well and the ratio of energy losses Δ/δ. Panel (b) shows Υ_{-1} as a function of the dimensionless quantum action $\alpha = \hbar\beta\lambda^{\ddagger}$ and δ for $\Delta/\delta = 4$.

factor Υ_{-1} typically increases when quantum tunneling comes into play. For larger energy loss ratios Δ/δ than shown here and sufficiently large δ, the depopulation factor has a shallow minimum as a function of α if δ is kept fixed at a sufficiently large value.

Fig. 3 shows the ratio of the direct rate from the left well to the right well to the total rate out of the left well: $Z = \Upsilon_{1\leftarrow -1}/\Upsilon_{-1}$, in the classical limit. For a fixed value of δ this ratio reaches a plateau for sufficiently large Δ/δ. The height of the plateau increases to unity with decreasing δ, since in this limit, the particle hardly gets trapped in the middle well.

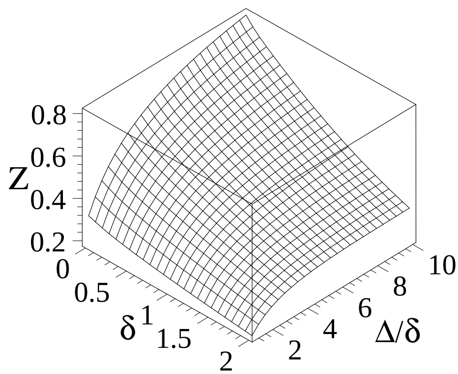

Fig. 3. The ratio $Z = \Gamma_{1\leftarrow -1}/\Gamma_{-1}$ of the partial rates from one to the other deep well and from a deep to the middle well as a function of δ and Δ/δ in the classical limit.

One may also compare the rates in the triple well system with the rate in a symmetric double well system with the same energy loss in each well as in the left and right wells of the triple well system. The corresponding depopulation factor for a double well system is given by [5]:

$$\Upsilon_{\rm dw} = \exp\left(\frac{\hbar\beta\lambda^{\ddagger}\sin(\hbar\beta\lambda^{\ddagger}/2)}{2\pi}\int_{-\infty}^{\infty} d\tau \frac{\ln\frac{1-\tilde{P}(-i(\tau+\frac{1}{2}))}{1+\tilde{P}(-i(\tau+\frac{1}{2}))}}{\cosh(\tau\hbar\beta\lambda^{\ddagger}) - \cos(\hbar\beta\lambda^{\ddagger}/2)}\right). \tag{2.25}$$

In Fig. 4 the total rate out of the left well relative to the double well rate is shown as a function of δ and Δ/δ in the classical limit. If the energy losses in the left and right wells and the middle well are comparable, this ratio is larger than unity by up to 40%. Otherwise it is close to unity with a shallow trench at small δ where the ratio of the rates is even less than unity.

Only a part of the particles escaping from the left well will finally enter the right well. If the rate out of the middle well is sufficiently fast half of those particles which enter the middle well will continue to the right well but

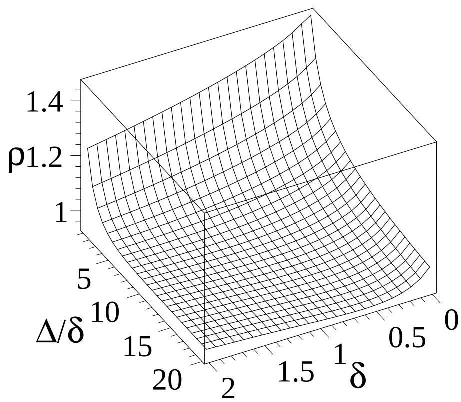

Fig. 4. The ratio $\rho = \Gamma_{-1}/\Gamma_{dw}$ of the total rate out of a deep well in a symmetric triple well system and in a double well system as a function of δ and Δ/δ in the classical limit.

the other half will go back to the left well. So the effective rate populating the right well is given by

$$\Gamma_{\to 1} = \Gamma_{1\leftarrow -1} + \tfrac{1}{2}\Gamma_{0\leftarrow -1}\,. \tag{2.26}$$

Panel (a) of Fig. 5 displays the ratio $\Gamma_{\to 1}/\Gamma_{dw}$ in the classical limit. One finds that it is a decreasing function in both arguments δ and Δ/δ which is always less than unity and goes to a half if either argument becomes large. If tunneling comes into play the effective rate is further decreased relative to the double well rate. In any case, the effective reaction rate is always suppressed by the presence of a third well.

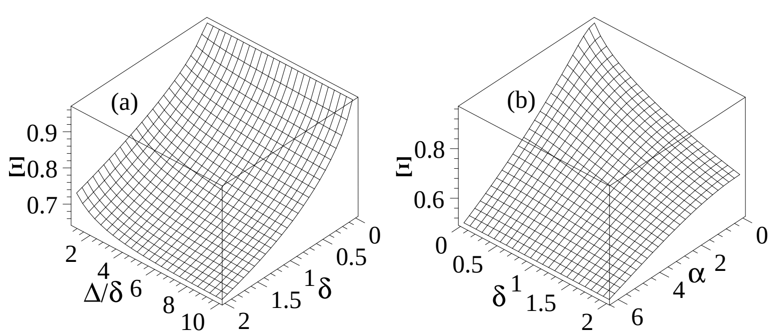

Fig. 5. Panel (a) displays the ratio $\Xi = \Gamma_{\to 1}/\Gamma_{dw}$ of the effective rate into the final deep well in the triple well system and of the double well rate in the classical limit as function of δ and Δ/δ. In panel (b) Ξ is shown as a function of the dimensionless action quantum α and δ at the fixed value $\Delta/\delta = 4$.

3. Discussion

A semiclassical solution for the rates in a symmetric triple well potential has been presented. The main result is that the presence of a middle well reduces the rate from left to right, relative to the double well case. At most, this reduction is by a factor of two. This occurs in the spatial diffusion limited regime, where the flux out of the left well first gets trapped in the middle well and only then has a probability of $1/2$ of reaching the right well. In the underdamped limit, if the energy loss in the middle well is small and sufficiently smaller than the energy loss in the left and right wells, then most of the escaping flux goes directly from left to right and the middle well becomes unimportant. The double hops lead to a larger rate then in the spatial diffusion limited regime where only single hops between adjacent wells can occur.

Quantum effects tend to always push one towards the spatial diffusion limited regime. Quantum tunneling reduces the energy needed for escape and thus the energy transfer process needed for activating the escaping particle becomes less important. As a result, the reduction of the rate due to the middle well grows in the presence of quantum tunneling.

The case studied here sheds light on what would happen in the case of a bridged system with N wells between the left and right deep wells. In the spatial diffusion limited regime, the rate is reduced by a factor of $1/(N+1)$ relative to the double well case [15]. In the underdamped limit, multiple hops over the bridge wells would ultimately bring the rate back to that expected for a double well potential. A solution of the general bridge potential problem is though much tougher and is left as an open problem for future research.

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