Transition Path Time Distribution, Tunneling Times, Friction, and Uncertainty

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A quantum mechanical transition path time probability distribution is formulated and its properties are studied using a parabolic barrier potential model. The average transit time is well defined and readily calculated. It is smaller than the analogous classical mechanical average transit time, vanishing at the crossover temperature. It provides a direct route for determining tunneling times. The average time may be also used to define a coarse grained momentum of the system for the passage from one side of the barrier to the other. The product of the uncertainty in this coarse grained momentum with the uncertainty in the location of the particle is shown under certain conditions to be smaller than the $\hbar/2$ formal uncertainty limit. The model is generalized to include friction in the form of a bilinear interaction with a harmonic bath. Using an Ohmic friction model one finds that increasing the friction, increases the transition time. Only moderate values of the reduced friction coefficient are needed for the quantum transition time and coarse grained uncertainty to approach the classical limit which is smaller than $\hbar/2$ when the friction is not too small. These results show how one obtains classical dynamics from a pure quantum system without invoking any further assumptions, approximations, or postulates.

The transition path time distribution has received much attention in recent years, especially in the context of protein folding [1–5]. The distribution provides the probability that a transition between two points in space of a molecular system (the protein) will take a time t. The most recent experiments of Neupane *et al.* have demonstrated that the distribution is measurable [6]. Moreover, the fit to a theoretical expression for the distribution was remarkably good. The theory thus far has been classical mechanical in nature, based on dissipative motion on a parabolic barrier potential [3–5]. For proteins, the friction is strong, the dynamics is well described within a Smoluchowski limit where quantum effects are unimportant [7]. However, the classical theory has raised the challenge of formulating a quantum theory for the transition path time distribution. This distribution is in principle a measurable quantity, for example, by the experimentally implemented imaging of a single atom in a time-of-flight experiment [8], albeit, the spatial resolution is diffraction limited. A different approach may be to measure recollision times in high harmonic generation [9].

A second aspect of interest has to do with the concept of time in quantum mechanics. The history of the definition of time and a time operator in quantum mechanics is rich [10–12]. It is of special interest in the context of tunneling times, where various theoretical approaches have shown that this time is either very small or vanishing [13–16]. Measurement of the tunneling time has remained, though, an enigma as summarized in Ref. [17]: "the assumption that tunneling has a well defined duration, …, would lead to a contradiction." A transition path time distribution could (as shown below) provide a different paradigm for the study of tunneling times.

Third, violations of the Heisenberg uncertainty principle and its precise definition have been the topic of numerous experimental and theoretical investigations in recent years [18–20]. The transition path time distribution is also relevant here. The average quantum time for the transition between two points, may be used to define an averaged coarse grained momentum for the transition. The natural question to arise then is whether this coarse grained momentum obeys any uncertainty principle.

In this Letter, we derive a quantum mechanical transition path time distribution for a parabolic barrier in the presence of dissipation. For a one-dimensional parabolic barrier (with barrier frequency $\omega^{\ddagger}$) one finds that the average transition time is a bell shaped function of the inverse temperature β [with $\beta = 1/(kT)$]. It vanishes at the so-called crossover temperature [21] for which $\hbar\beta\omega^{\ddagger} = 2\pi$. Introducing dissipation in the form of bilinear coupling to a harmonic bath [22] allows one to study the properties of the transition time distribution as a function of friction. This provides a direct demonstration of how friction affects a tunneling time [22]. One finds that the average transit time is an increasing function of the friction, reaching the classical limit already in the moderate friction limit. This sheds light on the question of how does a quantum system lose its quantum features. The model studied in this Letter is exactly quantum mechanical, yet when the friction is sufficiently large, the particle behaves classically. The quantum transition path time distribution provides a direct route from quantum mechanics to classical mechanics, without resorting to any external measurement process [23] or a theory of collapse [24,25].

The transition path time distribution for a one-dimensional Hamiltonian $\hat{H}$ (hats denote operators) will be defined as

$$P(t; x, y) = N \text{Tr} \left[\delta(\hat{q} - y) \exp\left(\frac{i\hat{H}t}{\hbar}\right) \hat{\rho}(x) \exp\left(-\frac{i\hat{H}t}{\hbar}\right) \right], \quad (1)$$

where N is a normalization constant. $\hat{\rho}(x)$ is a thermal density operator localized around the point x

$$\hat{\rho}(x) = \exp\left(-\frac{\beta\hat{H}}{2}\right) \delta(\hat{q} - x) \exp\left(-\frac{\beta\hat{H}}{2}\right) \quad (2)$$

chosen such that the transition path time distribution is symmetric with respect to inversion of the points x and y and such that it is positive for all times.

This present definition of the thermal distribution [Eq. (2)] differs from the standard thermodynamic definition which in its symmetrized version is $\hat{\rho}_S(x) = \frac{1}{2}[\exp(-\beta\hat{H})\delta(\hat{q} - x) + \delta(\hat{q} - x)[\exp(-\beta\hat{H})]$. Elsewhere [26] it is noted that the mean time of the distribution given in Eqs. (1) and (2) is identical to the mean time obtained using the standard definition for the thermal density. There is also a direct relation between the higher moments of the distributions based on the two definitions. The form used here [Eq. (2)] has the distinct advantage that $P(t; x, y)$ is positive for all times and so is a well-defined probability distribution.

The thermal density defined in Eq. (2) is also directly related to rate theory. Miller *et al.* [27] derived a thermal left-side correlation function whose time derivative at long times gives the reactive flux over a barrier. It is just a double spatial integral of the correlation function of Eqs. (1) and (2).

In this Letter, we first consider a one-dimensional parabolic barrier Hamiltonian for a particle with mass M and $\hat{p}$, $\hat{q}$ are the momentum and coordinate operators:

$$\hat{H} = \frac{\hat{p}^2}{2M} - \frac{M\omega^{\ddagger 2}\hat{q}^2}{2}. \quad (3)$$

The parabolic barrier is ubiquitous for almost all reactions occurring on a single adiabatic Born-Oppenheimer potential energy surface and so has a special place in the theory of chemical reaction dynamics. Not less important is that one of the objectives of the present Letter is to consider a system where one may derive analytic results without resorting to approximations. This is especially important when considering the intriguing question of tunneling times.

Since the configuration space matrix element for the propagator of quadratic Hamiltonians is known [28], one readily finds (N_{xy} is the normalization constant)

$$P(t; x, y)$$
$$= N_{x,y} \sqrt{\frac{1}{\sinh^2(\omega^{\ddagger}t) + \sin^2\left(\frac{\beta\hbar\omega^{\ddagger}}{2}\right)}}$$
$$\times \exp\left[-\frac{M\omega^{\ddagger}\sin(\beta\hbar\omega^{\ddagger})\left(x^2 + y^2 - \frac{2xy\cosh(\omega^{\ddagger}t)}{\cos\left(\frac{\beta\hbar\omega^{\ddagger}}{2}\right)}\right)}{2\hbar[\sinh^2(\omega^{\ddagger}t) + \sin^2\left(\frac{\beta\hbar\omega^{\ddagger}}{2}\right)]} \right]. \quad (4)$$

To simplify, we will consider the symmetric case $(y = -x)$. Using the reduced variables $\bar{t} = \omega^{\ddagger}t$, $\bar{\beta} = \beta\hbar\omega^{\ddagger}$, $Q = \frac{M\omega^{\ddagger 2}x^2}{2\hbar\omega^{\ddagger}}$ (Q will be referred to as the reduced barrier height) the symmetric distribution simplifies to

$$P_{\text{sym}}(\bar{t}) = N_{x,-x} \sqrt{\frac{1}{\sinh^2(\bar{t}) + \sin^2\left(\frac{\bar{\beta}}{2}\right)}}$$
$$\times \exp\left[\frac{-4\sin\left(\frac{\bar{\beta}}{2}\right)Q}{[\cosh(\bar{t}) - \cos\left(\frac{\bar{\beta}}{2}\right)]} \right]. \quad (5)$$

The time-dependent distribution may then be used to determine the nth moment of the distribution $\langle \bar{t}^n(x, y) \rangle = \int_0^\infty d\bar{t}\,\bar{t}^n P(\bar{t}; x, y)$ and the standard deviation $\langle \Delta\bar{t}(x, y) \rangle = \sqrt{\langle \bar{t}^2 \rangle - \langle \bar{t} \rangle^2}$. In the classical limit $\hbar \to 0$ one finds the symmetric normalized distribution

$$P_{\text{sym,cl}}(\bar{t}) = \frac{2}{\sinh(\bar{t})\text{Ei}(1, \beta V^{\ddagger})} \exp\left(-\beta V^{\ddagger}\coth^2\left(\frac{\bar{t}}{2}\right)\right) \quad (6)$$

where $\text{Ei}(1, \beta V^{\ddagger})$ is the exponential integral and $V^{\ddagger} = M\omega^{\ddagger 2}x^2/2$ is the "barrier height" and $\beta V^{\ddagger} = \bar{\beta}Q$.

The (reduced) average time of the transition as a function of the inverse temperature $\bar{\beta}$ for the reduced barrier heights $Q = 0.1, 1, 10$ is plotted in Fig. 1. The dotted lines show the respective classical values. Initially, decreasing the
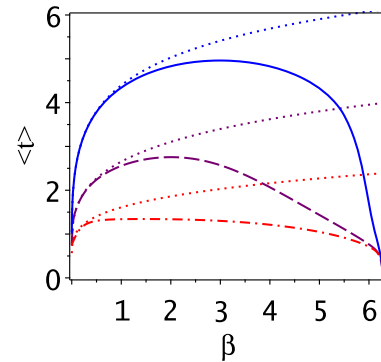

FIG. 1. Average transition time for thermal motion over a parabolic barrier. The solid (blue), dashed (purple) and dashed dotted (red) lines correspond to a reduced barrier height $Q = 10, 1, 0.1$, respectively. The dotted lines show the classical average times for each of the three cases. $\beta = \hbar\omega^{\ddagger}/(k_B T)$ is the reduced inverse temperature, the average time is dimensionless, in units of $\omega^{\ddagger}t$.

temperature increases the average transition time. This is the expected classical result, as the barrier height $\beta V^{\ddagger}$ increases the transit time should increase. But when the temperature is further lowered, tunneling kicks in and the quantum transit time becomes shorter than the classical going to 0 at the crossover point $\bar{\beta}_c = 2\pi$. One finds that for $\bar{\beta} = 2\pi - \varepsilon$, $\lim_{\varepsilon \to 0_+} \langle \bar{t} \rangle = -[\pi^2/4 \ln(\varepsilon)] \to 0$.

For the thermal quantum parabolic barrier the averaged transition time from one side of the barrier to the other has two contributions. One is from above barrier energies with times that are essentially classical. The other contribution is from tunneling which occurs in vanishing time. At the crossover temperature, one has tunneling contributions from all negative energies and these dominate to give a zero average tunneling time. In reality, one never has a parabolic barrier extending to $-\infty$ and one would have to consider the effects of nonlinearity of the potential on the transition time.

One may use the average time to estimate a coarse grained momentum of the particle and its uncertainty product. For the symmetric case of a transition from $-x$ to x this takes the form

$$\langle p \rangle = \frac{2Mx}{\langle t \rangle}, \qquad \langle \Delta p \rangle = \frac{1}{2} \left[\frac{2Mx}{\langle t \rangle - \langle \Delta t \rangle} - \frac{2Mx}{\langle t \rangle + \langle \Delta t \rangle} \right]. \tag{7}$$

The uncertainty in the position is $\langle \Delta q \rangle = 2x$. One may then evaluate the uncertainty product

$$U = \frac{2x\langle \Delta p \rangle}{\hbar} = \frac{8Q\langle \Delta \bar{t} \rangle}{\langle \bar{t} \rangle^2 - \langle \Delta \bar{t} \rangle^2} \tag{8}$$

and ask whether $U \geq 1/2$. This is shown in Fig. 2 where the uncertainty product is plotted as a function of the inverse temperature $\bar{\beta}$ for the reduced barrier heights $Q = 1, 10$. As in the previous figure, the classical values
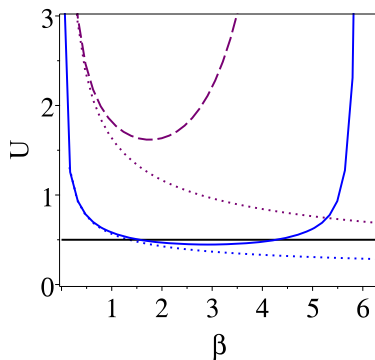

FIG. 2.   The uncertainty product for a thermal parabolic barrier. The notation is as in Fig. 1. The $Q = 0.1$ case is not shown since the uncertainty product is for all β much larger and outside of the range of the figure.

of the uncertainty product are plotted as dotted lines. For high temperature (small $\bar{\beta}$), the quantum and classical uncertainty products are similar. As the temperature is lowered, the classical uncertainty becomes smaller and goes below the $1/2$ mark. For $Q = 10$ the quantum uncertainty also becomes less than $1/2$ in the region where inspection of Fig. 1 shows that the average transition time is maximal. At lower temperatures, tunneling kicks in, the transit time becomes shorter, and the uncertainty again becomes larger than $1/2$. Increasing the barrier height would further increase the average transition time and thus reduce even more the uncertainty product in the turnover region. When considering coarse grained quantities, there is no uncertainty limit.

We now introduce dissipation such that the system is bilinearly coupled to a harmonic bath [22]:

$$\hat{H} = \frac{\hat{p}^2}{2M} + V(\hat{q}) + \frac{1}{2} \sum_{j=1}^{N} \left[\hat{p}_j^2 + \omega_j^2 \left(\hat{x}_j - \frac{\sqrt{M}c_j}{\omega_j^2} \hat{q} \right)^2 \right]. \tag{9}$$

The jth harmonic bath oscillator has mass weighted coordinate and momentum operators $\hat{x}_j$, $\hat{p}_j$ and associated frequency ω_j. It is well known [22] that in the classical limit, this Hamiltonian is equivalent to a generalized Langevin equation, with the friction function $\gamma(t) = \sum_{j=1}^{N} (c_j^2/\omega_j^2) \cos(\omega_j t)$. Since the dissipative Hamiltonian is quadratic, it may be diagonalized [29]:

$$\hat{H} \equiv \hat{H}_\rho + \hat{H}_B = \frac{\hat{p}_\rho^2}{2} - \frac{1}{2} \lambda^{\ddagger 2} \hat{\rho}^2 + \frac{1}{2} \sum_{j=1}^{N} [\hat{p}_{y_j}^2 + \lambda_j^2 \hat{y}_j^2] \tag{10}$$

where the jth stable normal mode oscillator (with frequency λ_j) has coordinate and momentum operators $\hat{y}_j$, $\hat{p}_{y_j}$ and $\hat{\rho}$, $\hat{p}_\rho$ are the mass weighted coordinate and momentum operators of the unstable normal mode. $\lambda^{\ddagger}$ is the unstable mode barrier frequency, expressed in terms of the Laplace transform of the time dependent friction $[\hat{\gamma}(s) = \int_0^\infty dt e^{-st} \gamma(t)]$ as the positive solution of the Kramers-Grote-Hynes equation [30,31]

$$\lambda^{\ddagger 2} + \lambda^{\ddagger} \hat{\gamma}(\lambda^{\ddagger}) = \omega^{\ddagger 2}. \tag{11}$$

Some additional properties of the normal mode Hamiltonian are that the projection u_{00} of the system coordinate (q) on the unstable normal mode ρ is given in the continuum limit through the relation [32]

$$u_{00}^2 = \left[1 + \frac{1}{2} \left(\frac{\hat{\gamma}(\lambda^{\ddagger})}{\lambda^{\ddagger}} + \left. \frac{\partial \hat{\gamma}(s)}{\partial s} \right|_{s=\lambda^{\ddagger}} \right) \right]^{-1}. \tag{12}$$

The spectral density of normal modes [33]

$$I(\lambda) = \frac{\pi}{2} \sum_{j=1}^{N} \frac{u_{j0}^2}{\lambda_j} [\delta(\lambda - \lambda_j) - \delta(\lambda + \lambda_j)] \tag{13}$$

(u_{j0} is the projection of the system coordinate (q) on the jth stable normal mode coordinate y_j) may be expressed in the continuum limit in terms of the Laplace transform of the time-dependent friction by the relation [34]

$$I(\lambda) = \lambda \mathrm{Re}[\hat{K}(i\lambda)] = \frac{\lambda \mathrm{Re}[\hat{\gamma}(i\lambda)]}{(\omega^{\ddagger 2} + \lambda^2)^2 + \lambda^2 \hat{\gamma}(i\lambda)\hat{\gamma}(-i\lambda)}. \quad (14)$$

The transition path time distribution is defined as in Eqs. (1) and (2) except that now the Hamiltonian is the full dissipative Hamiltonian of Eq. (10) and the Trace operation is over all variables, system, and bath. We then use the notations

$$\overline{G}_c = \sum_{j=1}^{N} \frac{u_{j0}^2}{\lambda_j} \coth\left(\frac{\beta\hbar\lambda_j}{2}\right) - \frac{u_{00}^2 \cos\left(\frac{\beta\hbar\lambda^{\ddagger}}{2}\right)}{\lambda^{\ddagger} \sin\left(\frac{\beta\hbar\lambda^{\ddagger}}{2}\right)}, \quad (15)$$

$$\overline{H}_s(t) = \sum_{j=1}^{N} \frac{u_{j0}^2 \cos(\lambda_j t)}{\lambda_j \sinh\left(\frac{\beta\hbar\lambda_j}{2}\right)} - \frac{u_{00}^2 \cosh(\lambda^{\ddagger} t)}{\lambda^{\ddagger} \sin\left(\frac{\beta\hbar\lambda^{\ddagger}}{2}\right)} \quad (16)$$

to find, after some manipulations and Gaussian integrations, the result for the transition path time distribution in the presence of friction:

$$P_{\mathrm{diss}}(t; x, y) = N_{\mathrm{diss}} \left(\frac{1}{[\overline{H}_s^2(t) - \overline{G}_c^2]}\right)^{1/2}$$
$$\times \exp\left(-\frac{M[\overline{G}_c(y^2 + x^2) - 2\overline{H}_s(t)yx]}{\hbar[\overline{G}_c^2 - \overline{H}_s^2(t)]}\right) \quad (17)$$

which for the symmetric case, simplifies to

$$P_{\mathrm{diss}}(t; -x, x) = N_{\mathrm{diss}} \left(\frac{1}{[\overline{H}_s^2(t) - \overline{G}_c^2]}\right)^{1/2}$$
$$\times \exp\left(-\frac{2Mx^2}{\hbar[\overline{G}_c - \overline{H}_s(t)]}\right). \quad (18)$$

The continuum limit of $\overline{G}_c$ and $\overline{H}_s(t)$ is readily obtained by employing the spectral density of the normal modes so that the sums are replaced by integrations over the variable λ. The classical limit of the distribution is obtained by taking the $\hbar \to 0$ limit of Eqs. (15), (16), and (18).

To obtain further insight we consider the transition path time distribution for Ohmic friction $\gamma(t) = 2\gamma\delta(t)$ where γ is the friction coefficient and $\delta(t)$ is the Dirac "delta" function. The average (reduced) transition time $\langle \omega^{\ddagger} t \rangle$ is plotted in Fig. 3 as a function of the reduced friction parameter $(\gamma/\omega^{\ddagger})$ for the barrier heights $Q = 0.1, 1, 10$, and the (reduced) inverse temperature $\overline{\beta} = 6$. The respective dotted lines show the classical average transition times for the respective reduced barrier values $\beta V^{\ddagger} = 0.6, 6, 60$. For $\overline{\beta} = 6$, one is very close to the crossover point ($\overline{\beta} = 2\pi$), so
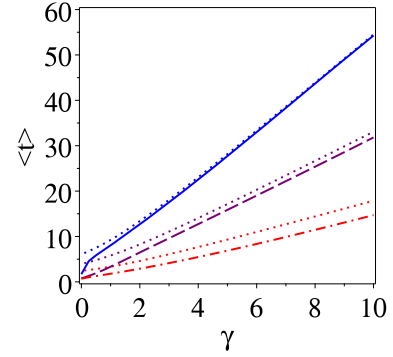

FIG. 3. Average transition time for thermal motion over a parabolic barrier coupled to an Ohmic bath is plotted as a function of the (reduced) friction parameter. Other notation is as in Fig. 1.

that without dissipation, the average transit time at $\overline{\beta} = 6$ almost vanishes. Turning on the friction coefficient increases the transit time, and as may be seen for moderate to large friction, the magnitude of $\overline{\beta}$ is almost of no relevance, the average transit time is very close to the classical result. Perhaps most significant is the fact that it does not take much friction for the quantum system to turn classical. In all three cases shown in the figure, which span 2 orders of magnitude in (reduced) barrier heights, the classical limit was more or less reached for (reduced) friction coefficients of 3 or more.

The rapid approach to the classical transition time with increasing friction indicates that the coarse grained uncertainty would also be smaller than $1/2$ as the friction is increased. This is shown in Fig. 4 where the uncertainty product [Eq. (8)] is plotted as a function of the friction coefficient for the inverse temperature $\overline{\beta} = 6$ and the barriers $Q = 0.1, 1, 10$. The classical uncertainty is represented by the dotted lines. The respective uncertainty drops below $1/2$ at $\overline{\gamma} \approx 4, 3, 7$. The quantum uncertainty is always larger than the classical; however, as the friction increases, the differences become small.
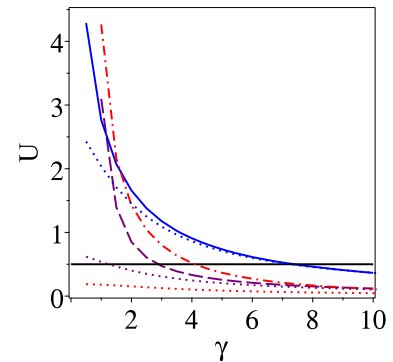

FIG. 4. The uncertainty product for a thermal parabolic barrier coupled to an Ohmic bath is plotted as a function of the (reduced) friction parameter. Other notation is as in Fig. 1.

In summary, there are a number of results presented in this Letter which are not specific to a parabolic barrier. First, the usage of a thermal density correlation function gives a precise determination of a transit time. In contrast to our previous definition of time in terms of flux correlation functions [35] where the flux correlation function is complex, the present usage of a density correlation function leads to a well-defined probability distribution for all times. The resulting mean transition times is a true mean. In the presence of tunneling, this transit time is shorter than the classical transit time, reflecting the fact that tunneling is either instantaneous or very fast. Second, by defining a coarse grained momentum one finds that even a quantum system may be localized more than expected from the uncertainty principle. Third, by coupling the system to a dissipative bath we have seen that dissipation increases the transit time, and tends to localize the quantum system. Surprisingly, it does not take too much friction to effectively turn the dynamics into classical.

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