Coherent Classical-Path Description of Deep Tunneling

Dong H. Zhang[1,2] and Eli Pollak[3]

[1]Center for Theoretical and Computational Chemistry and State Key Laboratory of Chemical Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, People's Republic of China 116023

[2]Department of Computational Science, National University of Singapore, Singapore 119260

[3]Chemical Physics Department, Weizmann Institute of Science, 76100, Rehovot, Israel

(Received 13 April 2004; published 27 September 2004)

A central challenge to the semiclassical description of quantum mechanics is the quantum phenomenon of "deep" tunneling. Here we show that real time classical trajectories suffice to account correctly even for deep quantum tunneling, using a recently formulated semiclassical initial value representation series of the quantum propagator and a prefactor free semiclassical propagator. Deep quantum tunneling is effected through what we term as coherent classical paths which are composed of one or more classical trajectories that lead from reactant to product but are discontinuous along the way. The end and initial phase space points of consecutive classical trajectories contributing to the coherent path are close to each other in the sense that the distance between them is weighted by a coherent state overlap matrix element. Results are presented for thermal and energy dependent tunneling through a symmetric Eckart barrier.

DOI: 10.1103/PhysRevLett.93.140401 PACS numbers: 03.65.Sq, 03.65.Xp

Tunneling is one of the most fascinating aspects of quantum mechanics. A (Gaussian) wave packet, localized initially on one side of a barrier with a mean energy and an energy variance substantially smaller than the barrier height is scattered off the barrier, but parts of it are transmitted through the barrier. This is a classically disallowed process; classical trajectories whose energy is below the barrier will of course be reflected by it. Yet the semiclassical description of quantum mechanics has come up with a variety of beautiful scenarios for "explaining" quantum tunneling with the aid of classical mechanics.

Perhaps the simplest approach is to represent the initial wave packet in phase space through its Wigner transform and then propagate it classically in time. The wave packet will always have a tail whose energy is larger than the barrier height. Classical trajectories initiated at these phase space points will be transmitted since their energy is above the barrier. The probability for such a transmission is exponentially small and so one has a qualitative description of tunneling via classical trajectories [1]. In fact, this classical path description of tunneling is exact for a parabolic barrier. However, as noted by Maitra and Heller [2], it will fail for "deep" tunneling. When the barrier is not parabolic, or more specifically when it goes to a constant value at plus or minus infinity, then the classical path contribution becomes too small. Tunneling is then dominated by nonclassical paths connecting two manifolds of classical trajectories lying close to the separatrix between transmitted and reflected trajectories. Kay [3] reanalyzed the tunneling problem and showed that "good" estimates of the tunneling probability may be obtained with single trajectories, provided that one uses a SemiClassical Initial Value Representation (SCIVR) of the propagator with coherent states that have a complex time dependent width. Grossmann has recently shown [4] that an estimate of the tunneling probability of similar quality to that of Kay may be obtained by splitting the propagator into a product of two equal time propagators and then estimating each half time propagator using an SCIVR propagator. In his computation, tunneling was effected through a combination of two classical trajectory segments. Burant and Batista continued in this vein using time slicing of the propagator [5].

An alternative description of tunneling is through use of classical trajectories evolving on the upside down potential energy surface. The tunneling process is then envisaged as a classically allowed motion up to the barrier, an imaginary time trajectory running through the barrier, and then again a real time classical trajectory leading from the turning point to the asymptotic region [6]. This description necessitates the use of complex trajectories.

A compromise between these two approaches has been suggested by Ankerhold and Saltzer [7,8]. Tunneling is effected by "large" fluctuations between families of periodic orbits. This description leads to a good estimation of deep tunneling probabilities.

We will present here a perspective of deep tunneling, which may be considered in some sense to include a combination of Kay's [3] and Grossmann's [4] insights to the problem. The path leading from reactants to products is composed of segments of classical trajectories. The end point in phase space of one segment and the initial point of the following segment are close to each other, as determined by an overlap of coherent state matrix elements. We may thus describe deep tunneling as effected by "coherent classical paths" leading from reactants to products. The number of segments needed is a function of

 © 2004 The American Physical Society

the depth of the tunneling: the deeper the tunneling, the more segments one needs. In contrast to the previous semiclassical approaches, the coherent classical path description presented here leads to the exact quantum tunneling probability. The methodology is also readily applicable to systems with many degrees of freedom, although here we will limit ourselves to one-dimensional tunneling through a symmetric Eckart barrier $V(q) = V_0 \cosh^{-2}\frac{q}{q_0}$ with the Hamiltonian $H = p^2/2m + V(q)$.

Our starting point is a prefactor free SCIVR of the quantum propagator whose form is [9]:

$$\hat{K}_0(t) = \int_{-\infty}^{\infty} \frac{dpdq}{2\pi\hbar} e^{\frac{i}{\hbar}S(p,q,t)} |g(p, q, t)\rangle\langle g(p, q, 0)|, \quad (1)$$

and we use the "hat" notation to denote quantum operators. The coordinate representation of the coherent state at time t is

$$\langle x|g(p, q, t)\rangle = \left(\frac{\Gamma_r(p, q, t)}{\pi}\right)^{\frac{1}{4}} \exp\left\{-\frac{\Gamma(p, q, t)}{2}[x - q(t)]^2 + \frac{i}{\hbar} p(t)[x - q(t)]\right\}, \quad (2)$$

where $p(t), q(t)$ are the classically evolved to time t momentum and coordinate p and q. Since we are dealing with a scattering problem in which much of the motion is in the asymptotic region, we will choose the width parameter appropriate for a free particle, that is, $\Gamma(t) = \frac{\Gamma}{1+i\hbar\Gamma t}$ with Γ as yet an arbitrary positive number and Γ_r and Γ_i denote the real and imaginary parts of $\Gamma(t)$ respectively. The action is $S(p, q, t) = \int_0^t dt'[\frac{p(t')^2}{2m} - \tilde{V}[q(t')] - \frac{\hbar^2}{2}\Gamma_r(t')]$ and the coherent state averaged potential is defined as $\tilde{V}[q(t)] = (\frac{\Gamma_r(t)}{\pi})^{1/2} \times \int_{-\infty}^{\infty} dx e^{-\Gamma_r(t)[x-q(t)]^2} V(x)$. This specific form of the SCIVR propagator has the feature that on the average it obeys the Heisenberg equation of motion at each point in phase space and time [9]. At the initial time, it reduces to the identity operator and it is exact for free particle motion. If the width parameter is chosen to be a constant ($\Gamma(p, q, t) =$ const) then the propagator given in Eq. (1) is identical to Heller's frozen Gaussian SCIVR propagator [10].

The time evolution equation for the SCIVR propagator is readily seen to be [11]

$$i\hbar \frac{\partial \hat{K}_0}{\partial t} = \hat{H}\hat{K}_0 + \hat{C}, \quad (3)$$

where the correction operator is [9]

$$\hat{C}(t) = \int_{-\infty}^{\infty} \frac{dpdq}{2\pi\hbar} \Delta V(\hat{q}, t) e^{\frac{i}{\hbar}S(p,q,t)} |g(p, q, t)\rangle\langle g(p, q, 0)|, \quad (4)$$

and $\Delta V(\hat{q}, t) = \tilde{V}[q(t)] + V'[q(t)][\hat{q} - q(t)] - V(\hat{q})$. The formal solution of the time evolution equation is [12]

$$\hat{K}_0(t) = \hat{K}(t) + \frac{1}{i\hbar}\int_0^t ds \hat{K}(t - s)\hat{C}(s), \quad (5)$$

where $\hat{K}(t)$ is the exact quantum propagator which obeys the equation of motion $i\hbar\frac{\partial \hat{K}}{\partial t} = \hat{H}\hat{K}$ and $\hat{K}(0) = \hat{I}$. Expanding the exact propagator in a power series in the correction operator gives the SCIVR series representation of the exact propagator:

$$\hat{K}(t) = \sum_{j=0}^{\infty} \hat{K}_j(t), \qquad \hat{K}_n(t) = \frac{i}{\hbar}\int_0^t ds \hat{K}_{n-1}(t - s)\hat{C}(s), \qquad n \geq 1. \quad (6)$$

One then notes that, for example, the first order correction $\hat{K}_1(t)$ involves a trajectory evolving from time 0 to time s and then a second trajectory evolving from the time s to the time t. The final phase space point $p(s), q(s)$ of the first segment is related to the initial phase space point of the second segment (p', q') through the overlap

$$\langle g(p', q', 0)|g(p, q, s)\rangle = \left(\frac{4\Gamma\Gamma_r(s)}{[\Gamma + \Gamma(s)]^2}\right)^{\frac{1}{4}} e^{-\frac{1}{2[\Gamma+\Gamma(s)]}[\Gamma\Gamma(s)[q'-q(s)]^2 + \frac{[p'-p(s)]^2}{\hbar^2}] + \frac{i}{\hbar}\frac{\Gamma p(s)+\Gamma(s)p'}{\Gamma+\Gamma(s)}[q'-q(s)]}, \quad (7)$$

demonstrating that the coherent state overlap forces the final and initial points to be "close" to each other. In this sense, the sum of the two trajectories gives a "coherent" path which evolves up to the time t. Clearly the nth term in the SCIVR series revolves about a coherent path composed of $n + 1$ coherent trajectory segments. In this way, the exact propagator is decomposed into contributions of coherent paths, whose number of discontinuities is related to the order of the term in the series. From a practical point of view, we shall show below that typically one need not go beyond the first few terms in the SCIVR series to obtain a very good description of the deep tunneling process.

We first consider the thermal rate for transmission through the symmetric Eckart barrier. The formal expression for the rate is given in terms of the eigenfunctions $|\phi_{\pm F}\rangle$ of the symmetrized thermal flux operator $\hat{F}(q^{\neq}, \beta) = e^{-\beta\hat{H}/2}\frac{1}{2m}[\hat{p}\delta(\hat{q} - q^{\neq}) + \delta(\hat{q} - q^{\neq})\hat{p}]e^{-\beta\hat{H}/2}$. Here $q^{\neq}$ is the location of the dividing surface taken to be 0 for the symmetric Eckart barrier and $\beta = 1/k_B T$ is the inverse temperature. The eigenvalues of the operator are $\pm F$; for explicit expressions in terms of matrix elements of the Boltzman operator see, for example, Ref. [13]. For our purposes, we note that the flux eigenfunctions and eigenvalues are computed numerically accurately. The thermal tunneling factor (unity in the classical high temperature limit but greater than unity in the deep tunneling region) for the barrier transmission probability is then defined as:

$$\varkappa(\beta) = 2\pi\hbar\beta F \int_0^\infty dt C_F(t),$$
$$C_F(t) \equiv \left[\left\langle \phi_{+F} \middle| \hat{K}^\dagger(t)\hat{F}(q^\ddagger, 0)\hat{K}(t) \middle| \phi_{+F} \right\rangle - \left\langle \phi_{-F} \middle| \hat{K}^\dagger(t)\hat{F}(q^\ddagger, 0)\hat{K}(t) \middle| \phi_{-F} \right\rangle \right]. \quad (8)$$

where $\hat{K}(t) = e^{-i/\hbar(\hat{H}t)}$ is the exact quantum real time propagator and $C_F(t)$ is the thermal flux autocorrelation function.

Using the same parameters for the Eckart barrier as studied in Ref. [14], we plot in Fig. 1 the flux autocorrelation function for three different temperatures. The width parameter Γ was chosen optimally by minimizing the expectation value of the correction operator, as described in Ref. [15]. Panel (a) compares the numerically exact correlation function with the results obtained using the zeroth and first order terms in the SCIVR series at the (inverse) temperature $\hbar\beta\omega = 4$, which is well above the crossover temperature ($\hbar\beta\omega = 2\pi$) between thermal activation and below barrier tunneling. The tunneling factor at this temperature is $\varkappa(\beta) = 2.07$ and so perhaps it is not surprising that already the first order term converges to the exact result. Panel (b) of the figure shows the flux correlation function at a lower temperature $\hbar\beta\omega = 10$ for which the tunneling factor is $\varkappa(\beta) = 162$. Panel (c) shows the same but for very deep tunneling, the (inverse) temperature is $\hbar\beta\omega = 20$ and the tunneling factor is $\varkappa(\beta) = 5.34 \times 10^8$. Even for this deep tunneling case, deep in the sense that the temperature is well below the crossover temperature of $\hbar\beta\omega = 2\pi$, one sees that already the second term in the SCIVR series converges to the exact answer. As argued by Maitra and Heller, the zeroth order term is insufficient to give the correct tunneling factor. But adding in the coherent paths, which include one and two jumps between classical paths suffices for an excellent description of the tunneling dynamics. We note that the results presented in Fig. 1 are a rather stringent test for the SCIVR series method. Not only does the transmission factor come out correct but so does the time dependent flux correlation function.

It is also of interest to study the tunneling dynamics in the energy domain. In Fig. 2, we plot the energy dependent transmission probability for the same Eckart barrier. The probability is obtained by Fourier transformation of the time evolved thermal flux eigenfunction $|\phi_{+F}\rangle$ whose temperature was chosen to be $\hbar\beta\omega = 4$. The fact that the zeroth order term gives probabilities which are greater than unity should not be of any special concern. The

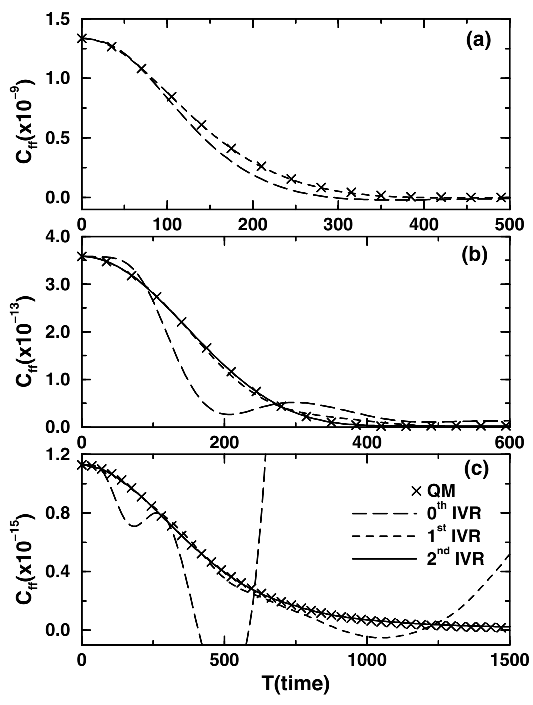

FIG. 1. The thermal flux autocorrelation function for an Eckart barrier at three different temperatures. Panels (a)-(c) correspond to the reduced inverse temperatures $\hbar\beta\omega = 4, 10, 20$, respectively. The notation for the various lines appears in the legend on the figure. For further details, see the text.

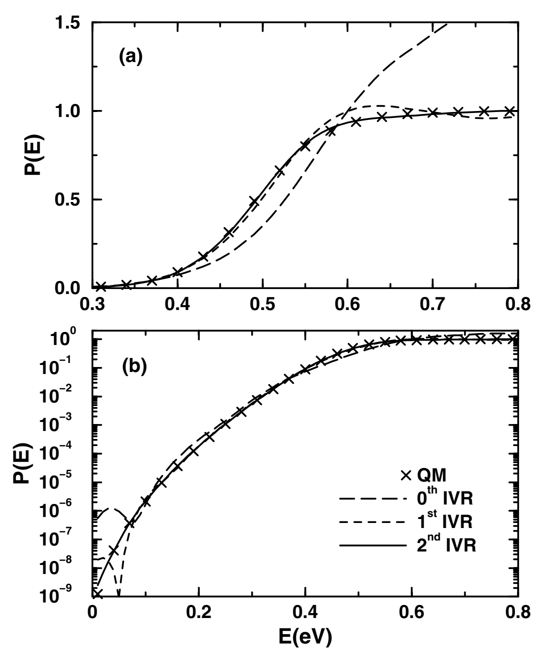

FIG. 2. The energy dependent transmission probability for a symmetric Eckart barrier. Panel (a) shows results on a linear scale, panel (b) on a logarithmic scale. The notation for the various lines appears in the legend on the figure. Note the convergence to the numerically exact result even in the low energy deep tunneling region.

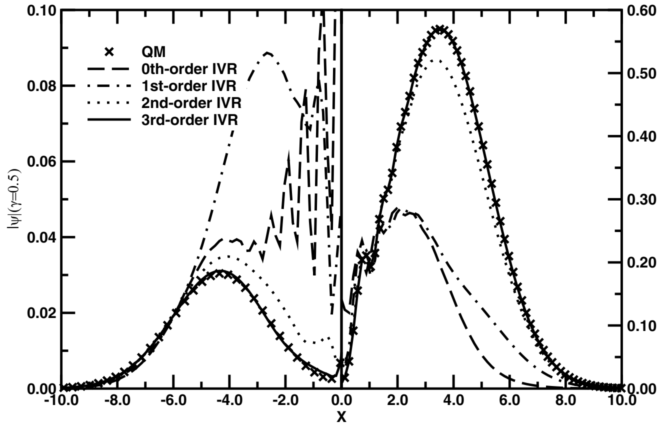

FIG. 3. Reflection and transmission of a Gaussian wave packet incident on a symmetric Eckart barrier from the right. The right panel of the figure shows the reflected wave packet, the left panel the transmitted. Note the change of scale in the amplitude for each panel. The notation of the lines appears in the legend on the figure. For other details, see the text.

SCIVR propagator is in general not a unitary operator. What is important to note is that for almost the whole energy range, it takes three terms in the SCIVR series to converge to the exact result. At the lowest energy shown (0.01 eV), the exact probability is 1.29×10^{-9}. Results based on the second, third and fourth order terms are 2.51×10^{-9}, 1.40×10^{-9}, and 1.31×10^{-9}, respectively. Since the second order term suffices for all other energies, we do not plot the higher order results in Fig. 2. We also stress that in all our computations, we have found that the SCIVR series is well behaved and one does not find any divergence when going to higher orders in the series.

Finally, in Fig. 3, we plot a time evolved Gaussian wave packet whose initial energy was half the barrier height (0.5 eV) and whose variance in space was 1.5 a.u., which implies an energy variance of 0.029 eV. The wave packet was initiated to the right of the barrier. Its fate after scattering is shown in the figure. Most of it is reflected as shown in the right panel. The amplitude of the transmitted part, shown in the left panel, is much smaller (note the change of scale in the figure). However, it takes only four terms in the SCIVR series to obtain the correct reflected and transmitted wave packet.

In summary, we have demonstrated that deep quantum tunneling is well described in terms of coherent classical paths which involve only real time classical trajectories. Tunneling occurs through coherent classical paths, consisting of a few trajectory segments related to each other by coherent state overlap matrix elements. Interestingly, even deep tunneling does not necessitate more that a few jumps in the path. We have employed a prefactor free SCIVR of the propagator. One could repeat the same computation using the Herman-Kluk propagator [16]. Past experience shows that this would lead to even faster convergence of the SCIVR series [9]. In other words, the number of trajectory segments needed to describe the tunneling does depend on the SCIVR propagator used. Since it is much more difficult to compute the Herman-Kluk propagator in many dimensions because of the prefactor, we limited ourselves here to the prefactor free propagator. Although this Letter deals only with one-dimensional tunneling, there is nothing in the SCIVR series method that limits its dimensionality in principle, and one should expect that the coherent classical path picture presented here will remain valid also for multi-dimensional tunneling problems.

We thank Professor J. Shao for stimulating discussions. This work has been supported by grants of the U.S. Israel Binational Science Foundation and the Israel Science Foundation. D. H. Zhang acknowledges an academic research grant from the Ministry of Education and Agency for Science and Technology Research, Republic of Singapore.

[1] S. Keshavamurthy and W. H. Miller, Chem. Phys. Lett. **218**, 189 (1994).
[2] N.T. Maitra and E.J. Heller, Phys. Rev. Lett. **78**, 3035 (1997).
[3] K. G. Kay, J. Chem. Phys. **107**, 2313 (1997).
[4] F. Grossmann, Phys. Rev. Lett. **85**, 903 (2000).
[5] J.C. Burant and V.S. Batista, J. Chem. Phys. **116**, 2748 (2002).
[6] T. F. George and W. H. Miller, J. Chem. Phys. **56**, 5722 (1972); *ibid.* **57**, 2458 (1972); W. H. Miller, J. Chem. Phys. **62**, 1899 (1975).
[7] J. Ankerhold and M. Saltzer, Phys. Lett. A **305**, 251 (2002).
[8] M. Saltzer and J. Ankerhold, Phys. Rev. A **68**, 042108 (2003).
[9] S. Zhang and E. Pollak, J. Chem. Phys. **121**, 3384 (2004).
[10] E. J. Heller, J. Chem. Phys. **75**, 2923 (1981).
[11] J. Ankerhold, M. Saltzer and E. Pollak, J. Chem. Phys. **116**, 5925 (2002).
[12] S. Zhang and E. Pollak, Phys. Rev. Lett. **91**, 190201 (2003).
[13] E. Pollak, J. Chem. Phys. **107**, 64 (1997).
[14] E. Pollak and B. Eckhardt, Phys. Rev. E **58**, 5436 (1998).
[15] S. Zhang and E. Pollak, J. Chem. Phys. **119**, 11058 (2003).
[16] M. F. Herman and E. Kluk, Chem. Phys. **91**, 27 (1984).