Trajectory Based Non-Markovian Dissipative Tunneling

Werner Koch,[1] Frank Grossmann,[1] and David J. Tannor[2]

[1]*Institut für Theoretische Physik, Technische Universität Dresden, D-01062 Dresden, Germany*

[2]*Department of Chemical Physics, The Weizmann Institute of Science, Rehovot, Israel*

(Received 26 August 2009; revised manuscript received 21 April 2010; published 3 December 2010)

The influence of a dissipative environment on scattering of a particle by a barrier is investigated by using the recently introduced Bohmian mechanics with complex action [J. Chem. Phys. **125**, 231103 (2006)]. An extension of this complex trajectory based formalism to include the interaction of the tunneling particle with an environment of harmonic oscillators with a continuous spectral density and at a certain finite temperature allows us to calculate transmission probabilities beyond the weak system bath coupling regime. The results display an increasing tunneling probability for energies below the barrier and a decreased transmission above the barrier due to the coupling. Furthermore, we demonstrate that solutions of a Markovian master equation fail to do so in general.

DOI: 10.1103/PhysRevLett.105.230405 PACS numbers: 03.65.Xp, 03.65.Yz, 05.40.−a, 74.50.+r

The past decades have seen a vast number of studies on quantum tunneling under the influence of environmental degrees of freedom [1,2]. The focus of interest has ranged from theoretical investigations on the dissipative quantum transmission in inverted harmonic [3–5], cosine [6], and (biased) rectangular barrier potentials [7,8] to theoretical as well as experimental work on dissipative nuclear fission and fusion [9,10], proton tunneling in solids [11], low temperature Josephson systems [12–14], all the way to electron transfer in biomolecules [15]. Three different barrier tunneling scenarios can be distinguished. Firstly, there is the coherent tunneling dynamics in a prototypical double-well potential. Describing the double well by its lowest two levels, in the presence of an environment, leads to the spin-boson Hamiltonian whose dynamics is reviewed in [16]. Secondly, a particle can tunnel out of a metastable well. With environmental coupling in the case of low temperatures, this leads to the quantum Kramers problem [1,17]. Thirdly, an initially free particle scattered from a short-range barrier potential gets partly reflected and transmitted. A central question in all dissipative tunneling studies is whether the environment enhances or suppresses the tunneling dynamics. Most authors seem to agree that transmission is increased by contact to the environment for incident energies below the barrier height (corresponding to true tunneling), whereas for incident energies above the barrier the transmission is suppressed [3,5,8–10]. It is not always simple, however, to disentangle the variety of approximations used and the differing system and bath parameters that have been applied in different works [5].

In order to provide a comprehensive study for a wide range of parameters, such as coupling strength, temperature, and initial energy, one has to start from a microscopic description of the composite system. Methods used to investigate barrier scattering in the presence of an environment include the Feynman-Vernon influence functional formalism [18,19], Lindblad-type Markovian master equations [5,20,21], the dynamical norm method [10], and the derivative propagation method [21]. These, however, are all limited to certain scenarios or parameter regimes.

In the following we will present a general scheme that allows for numerical evaluation of tunneling probabilities over a wide range of system parameters, even in the non-Markovian regime. It is based on the combination of trajectory based solutions of appropriate time-dependent Schrödinger equations [22] with a stochastic averaging procedure [23]. We restrict the presentation of numerical results to the barrier scattering case.

A quantum system in contact with an environment is frequently described by a Hamiltonian that can be split into three parts, according to

$$\hat{H}(t) = \hat{H}_S + \hat{H}_B + \hat{H}_I, \tag{1}$$

where $\hat{H}_S$, $\hat{H}_B$, and $\hat{H}_I$ denote system, bath, and interaction part, respectively. According to the Caldeira-Leggett model [12] the environmental degrees of freedom are taken to be harmonic and bilinearly coupled to the system coordinate. In addition, the initial condition for the density matrix of the composite system is frequently assumed to be factorizing. The resulting Feynman-Vernon influence functional for the reduced system density matrix [24] has proven to be discouragingly hard to deal with directly. It has recently been shown, however, that an exact formulation of the problem via a stochastic Liouville–von Neumann (SLN) equation is possible, where all the effects of the environment are recast into two complex-valued, Gaussian distributed, stochastic forces $\xi(t)$ and $\nu(t)$ acting on the system [23]. Thereby the *explicit* memory due to the environmental dynamics is removed, but all the non-Markovian effects are *implicitly* contained in the correlations of the noise distribution, $\mathfrak{M}[\xi(t)\xi(t')] = L'(t-t')$, $\mathfrak{M}[\xi(t)\nu(t')] = (2i/\hbar)\Theta(t-t')L''(t-t')$, and $\mathfrak{M}[\nu(t)\nu(t')] = 0$. Here $\mathfrak{M}$ is the probability measure of

the noise force distribution and $L(t) = L'(t) + iL''(t)$ is the kernel of the reservoir. For the Caldeira-Leggett model, this kernel can be computed in closed form and depends on the temperature and the spectral density of the bath oscillators [24]. Unraveling the forward and the backward path in the influence functional by stochastic driving forces, and writing the initial reduced density as a product of pure states $\hat{\rho}(t=0) = |\Psi_1\rangle\langle\Psi_2|$, the SLN equation leads to a set of two time-dependent Schrödinger equations (TDSEs) in Stratonovich form [23]:

$$i\hbar|\dot{\Psi}_1\rangle = \left[H_S - \xi(t)x + \frac{\mu}{2}x^2 - \frac{\hbar}{2}\nu(t)x\right]|\Psi_1\rangle \quad (2)$$

$$i\hbar|\dot{\Psi}_2\rangle = \left[H_S - \xi^*(t)x + \frac{\mu}{2}x^2 + \frac{\hbar}{2}\nu^*(t)x\right]|\Psi_2\rangle, \quad (3)$$

where $\mu = -\int_0^\infty du L''(u)/(2\hbar)$ is the static susceptibility of the reservoir. In [25] a thorough discussion of the nature of the noise, its numerical generation, and further technical issues can be found.

This non-Markovian unraveling of the bath's influence is *not* restricted to weak coupling and can in principle be combined with any TDSE propagation scheme. As shown in [26], trajectory based semiclassical propagators, like the Heller-Herman-Kluk-Kay propagator [27], allow stable computations over long propagation times—until thermalization is reached—with reasonable computational effort. The semiclassical propagator is unable, however, to handle tunneling problems, unless augmented by additional terms of an $\hbar$ expansion [28]. These additional terms, however, introduce a degree of complication into the numerical scheme that becomes prohibitive when combined with the averaging required for the stochastic modeling of the environment.

A more suitable trajectory based method, that can in principle be converged to the exact solution of the TDSE, and that therefore allows for the description of tunneling, is the recently developed Bohmian mechanics with complex action (BOMCA) [22]. As opposed to the traditional Bohmian approach to quantum mechanics, in BOMCA the wave function is written using a complex-valued exponentiated action field, containing both amplitude and phase. This leads to the ansatz

$$\Psi(\vec{x}, t) = \exp\left\{\frac{i}{\hbar}S(\vec{x}, t)\right\}, \qquad S: \mathbb{C}^d \times \mathbb{R} \to \mathbb{C}.$$

Upon inserting this wave function into the TDSE and adding the spatial terms containing the implicit time dependence, one obtains an ordinary differential equation (ODE) for the action $S(\vec{x}(t), t)$

$$\frac{dS}{dt} = -\frac{1}{2m}(\vec{\nabla}S)^2 - V(\vec{x}(t), t) + \frac{i\hbar}{2m}\vec{\nabla}^2 S + \frac{\partial\vec{x}}{\partial t}\frac{\partial S}{\partial\vec{x}}. \quad (4)$$

In order to integrate this quantity along a trajectory, one needs a way to evaluate spatial derivatives of $S(\vec{x}(t), t)$. In principle it is possible to propagate multiple trajectories and calculate the derivatives with a finite difference scheme [29]. An alternative approach is to calculate initial conditions for the spatial derivative of (4), and evaluate that quantity along the trajectory [22,30,31]. This in turn requires equations of motion for even higher derivatives which again can be obtained from further differentiating the resulting ODE. This leads to an infinite but closed hierarchy of ODEs for the spatial derivatives of $S(\vec{x}(t), t)$. For any practical calculation, however, a cutoff for the hierarchy at some order N is required.

In one dimension the procedure just outlined results in the following set of equations:

$$\frac{dS_n}{dt} = -\frac{1}{2m}(S_1^2)_n - V_n + \frac{i\hbar}{2m}S_{n+2} + \upsilon S_{n+1}, \quad (5)$$

$$S_{N+1} = S_{N+2} = 0, \quad (6)$$

$$(S_1^2)_n = \sum_{j=0}^{n}\binom{n}{j}S_{j+1}S_{n-j+1}, \quad (7)$$

where the subscript denotes the order of the derivative and runs from 0 to N. The quantities υ, S_n, and V_n depend on time and the coordinate of the trajectory $x(t)$. What remains to be specified is an expression for $\upsilon(x(t), t) \equiv \frac{dx}{dt}$ and the initial values for the derivatives of $S(x(t), t)$. The former is taken from the physical interpretation of $S(x(t), t)$ as the system's action

$$\upsilon(x(t), t) = \frac{S_1(x(t), t)}{m}, \quad (8)$$

and the latter from the ansatz for the initial wave function

$$S_n(x(t_i), t_i) = -i\hbar\frac{\partial^n}{\partial x^n}\ln\{\Psi(x, t_i)\}\Big|_{x=x(t_i)}. \quad (9)$$

The coordinates of the trajectories evolving due to the equation of motion (8) will, in general, acquire imaginary components or may even start on arbitrary points in the complex plane. The physical wave function needs to be evaluated on the real axis, however. Therefore, only trajectories with a purely real final coordinate are of physical interest, and a root search in the complex initial position space needs to be performed to identify those trajectories that do have a vanishing final imaginary component. Generally there will be more than one branch in the $x(t_i) \to x(t_f)$ map leading to the real axis. For tunneling transmission, however, there is just a single contribution to the final result. Furthermore, as has been shown in [22], a cutoff of the BOMCA hierarchy at order $N = 2$ is sufficient to accurately describe barrier transmission without coupling to the environment.

The stochastic force can be introduced into the above propagation scheme just like any other explicitly time-dependent force. In fact, the use of a complex-valued

driving force to simulate the coupling to the environment is quite natural since the BOMCA trajectories are complex valued by design. However, the root search becomes considerably more involved. It has to be redone for each noise sample, and special care has to be taken in dealing with the different branches of the $x(t_i) \to x(t_f)$ map. Nevertheless, in the following we show that the combination of both BOMCA and SLN dynamics is feasible. A noise sample count between 10^6 and 10^8 turned out to be sufficient to obtain converged results for coupling strength η [see Eq. (11) below] up to 0.5 and quasiconverged results for $\eta = 0.6$ and high temperatures.

As a numerical example we consider the scattering of an initial wave packet $\Psi(x, 0) = (\sigma/\pi)^{1/4} \exp\{-\sigma/2 (x - q_0)^2 + i p_0 (x - q_0)\}$, with width parameter $\sigma = 60\pi$ and initial center energy $E_0 = p_0^2/(2m)$, where $m = 30$, from a symmetric Eckart barrier potential

$$V(x) = \frac{D}{[\cosh(\beta x)]^2}, \tag{10}$$

where $\beta = 4.32$ was chosen for the range parameter and $D = 40$ for the barrier height and all quantities are in atomic units. The spectral density of the bath oscillators was chosen to be Ohmic with an algebraic cutoff

$$J(\omega) = \frac{\eta \omega}{(1 + \omega^2/\omega_c^2)^2}. \tag{11}$$

For all results presented in this Letter we chose the cutoff frequency to be $\omega_c = 10$.

For the barrier (10) located at $x = 0$, the quantity to be monitored is the transmission probability, that is

$$P(t_f) = \frac{\mathfrak{Tr} \int_0^\infty dx |x\rangle\langle x| \hat{\rho}(t_f)}{\mathfrak{Tr} \hat{\rho}(t_f)}, \tag{12}$$

evaluated at a time $t_f \to \infty$, long enough for the transmitted part of the wave packet to have passed well beyond the range of the barrier.

Figure 1 shows the dependence of the transmission probability on the incident energy E_0 of the wave packet and the coupling strength to the reservoir η for $q_0 = -0.7$ and a high temperature of $T = 400$. Compared to the uncoupled case, the transmission decreases for high energies $E \gtrsim D$, whereas it increases for low energies $E \lesssim D$ due to the environmental influence.

If the temperature of the heat bath is decreased for comparable coupling strength of $\eta = 0.4$, the results shown in Fig. 2 (again $q_0 = -0.7$) are obtained. Decreasing the temperature of the bath also decreases the change in transmission compared to the uncoupled case. To stress the non-Markovian nature of the observed effect, we have also performed calculations of the transmission probability using the Caldeira-Leggett high temperature master equation (CLME), which is based on Ohmic dissipation (see [32] for implementation details). These results, which are depicted by the dotted line in Fig. 2, show a qualitatively wrong influence of the environment on the tunneling dynamics at low temperatures, where they fail to predict the enhancement of tunneling for energies below the barrier.

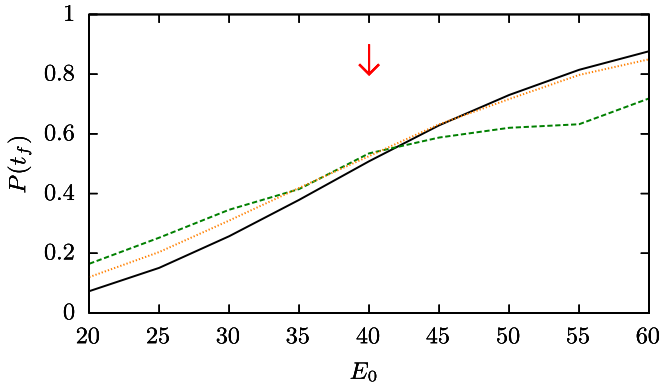

FIG. 1 (color online). Transmission probability versus energy for $\eta = 0$ (solid black line), $T = 400$, $\eta = 0.2$ (dotted orange line), $\eta = 0.6$ (dashed green line). BOMCA order $N = 4$.

The results presented in the two figures were obtained with $N = 4$ for the cutoff of the BOMCA hierarchy. It turns out that as η is increased, higher orders are needed to converge the results. To shed some more light on this point, in Table I we give values for the transmission for two exemplary points, $E = 20$ and $E = 60$ below, respectively, above the barrier maximum at an intermediate temperature of $T = 40$. The BOMCA results of different order are compared with split-operator fast-Fourier-transform (FFT) ones. For the lower damping strength both BOMCA results are already close to the full quantum result. At higher damping and for the larger energy the $N = 4$ results are much better than for $N = 2$. While not fully converged, $N = 4$ is still better than the CLME results. Fortunately, the numerical effort required to converge the low temperature BOMCA (non-Markovian) results is reduced as compared to the high temperature case.

So far we have considered the case $q_0 = -0.7$ for the initial wave packet center. If the wave packet is removed

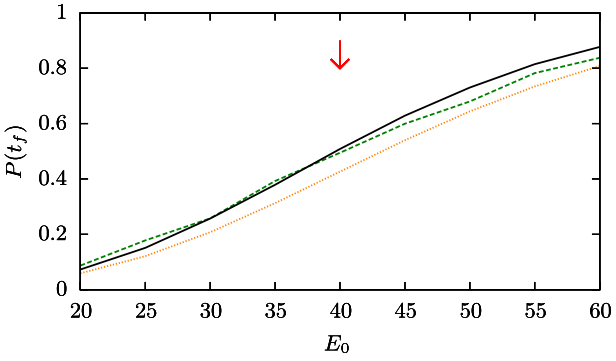

FIG. 2 (color online). Transmission probability versus energy for $\eta = 0$ (solid black line), $\eta = 0.4$, $T = 40$ CLME results (dotted orange line), BOMCA $N = 4$ results (dashed green line).

TABLE I. Transmission probability for $\eta = 0.4, 0.6$, $T = 40$ with different levels of BOMCA order compared to split-operator FFT and CLME results.

	$\eta = 0.4$				$\eta = 0.6$			
E	$N = 2$	$N = 4$	FFT	CLME	$N = 2$	$N = 4$	FFT	CLME
20	0.093	0.087	0.086	0.059	0.089	0.086	0.092	0.064
60	0.71	0.84	0.87	0.81	0.69	0.86	0.86	0.80

away from the barrier far enough for thermalization to set in already in the free particle dynamics [33], the dependence of the transmission probability on the incident energy is drastically reduced (not shown). The calculations of Figs. 1 and 2 were performed with $q_0 = -0.7$. This small distance from the barrier allows only partial thermalization of the wave packet and is thus equivalent to the introduction of a position dependent form factor in the interaction Hamiltonian as it is frequently done when considering dissipative tunneling [7,9,10,18].

Summarizing, we have shown that the dissipative dynamics described by a stochastic Liouville–von Neumann equation with complex noise forces can be combined with the trajectory based BOMCA method. This way tunneling processes under the influence of an environment can in principle be studied to the desired accuracy beyond weak coupling and in a strongly non-Markovian regime. We have demonstrated that the environmental influence on the transmission probabilities intimately depends on the initial state's position as well as on its energy in relation to the barrier height. The decrease of transmission probabilities for incident energies above the barrier height and the increase below it is reproduced by the proposed approach, whereas it cannot be reproduced in general by a Markovian master equation approach. With the proposed formalism the study of different kinds of tunneling dynamics in the presence of a heat bath is within reach. One promising direction of future research is to go beyond bilinear system bath coupling.

W. K. and F. G. gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft under projects GR 1210/4-1,2 and valuable discussions with J. Ankerhold, E. Pollak, J. T. Stockburger, and W. T. Strunz. D. J. T. gratefully acknowledges financial support by the Israel Science Foundation. This research is made possible in part by the historic generosity of the Harold Perlman family.

[1] P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990).
[2] U. Weiss, *Quantum Dissipative Systems* (World Scientific, Singapore, 2008), 3rd ed.
[3] A. Widom and T. D. Clark, Phys. Rev. Lett. **48**, 63 (1982).
[4] L. H. Yu, Phys. Rev. A **54**, 3779 (1996).
[5] A. Isar, A. Sandulescu, and W. Scheid, Eur. Phys. J. D **12**, 3 (2000).
[6] Y. Tanimura and P. G. Wolynes, J. Chem. Phys. **96**, 8485 (1992).
[7] M. Ueda, Phys. Rev. B **54**, 8676 (1996).
[8] K. Konno, M. Nishida, S. Tanda, and N. Hatakenaka, Phys. Lett. A **368**, 442 (2007).
[9] P. Fröbrich, R. Lipperheide, and K. Möhring, Z. Phys. B **78**, 325 (1990).
[10] N. Takigawa, K. Hagino, and M. Abe, Phys. Rev. C **51**, 187 (1995).
[11] H. Grabert and H. Wipf, in *Festkörperprobleme–Advances in Solid State Physics*, edited by U. Rössler (Vieweg, Braunschweig, 1990), Vol. 30, p. 1.
[12] A. O. Caldeira and A. J. Leggett, Ann. Phys. (N.Y.) **149**, 374 (1983).
[13] M. H. Devoret, J. M. Martinis, and J. Clarke, Phys. Rev. Lett. **55**, 1908 (1985).
[14] H. Grabert, P. Olschowski, and U. Weiss, Phys. Rev. B **32**, 3348 (1985).
[15] A. Garg, J. N. Onuchic, and V. Ambegaokar, J. Chem. Phys. **83**, 4491 (1985).
[16] A. J. Leggett *et al.*, Rev. Mod. Phys. **59**, 1 (1987).
[17] E. Pollak, Phys. Rev. A **33**, 4244 (1986).
[18] R. Bruinsma and P. Bak, Phys. Rev. Lett. **56**, 420 (1986).
[19] G. R. Haynes and G. A. Voth, Phys. Rev. A **46**, 2143 (1992).
[20] G. G. Adamian, N. V. Antonenko, and W. Scheid, Phys. Lett. A **244**, 482 (1998).
[21] K. H. Hughes and R. E. Wyatt, J. Chem. Phys. **120**, 4089 (2004).
[22] Y. Goldfarb, I. Degani, and D. J. Tannor, J. Chem. Phys. **125**, 231103 (2006).
[23] J. T. Stockburger and H. Grabert, Phys. Rev. Lett. **88**, 170407 (2002).
[24] R. P. Feynman and F. L. Vernon, Ann. Phys. (N.Y.) **24**, 118 (1963).
[25] W. Koch, F. Grossmann, J. T. Stockburger, and J. Ankerhold, Chem. Phys. **370**, 34 (2010).
[26] W. Koch, F. Grossmann, J. T. Stockburger, and J. Ankerhold, Phys. Rev. Lett. **100**, 230402 (2008).
[27] M. F. Herman and E. Kluk, Chem. Phys. **91**, 27 (1984).
[28] G. Hochman and K. G. Kay, J. Phys. A **41**, 385303 (2008).
[29] C. L. Lopreore and R. E. Wyatt, Phys. Rev. Lett. **82**, 5190 (1999).
[30] C. J. Trahan, K. Hughes, and R. E. Wyatt, J. Chem. Phys. **118**, 9911 (2003).
[31] J. Liu and N. Makri, J. Phys. Chem. A **108**, 5408 (2004).
[32] F. Grossmann and W. Koch, J. Chem. Phys. **130**, 034105 (2009).
[33] V. Hakim and V. Ambegaokar, Phys. Rev. A **32**, 423 (1985).