

The Flux-Flux Correlation Function for Anharmonic Barriers

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(Dated: September 27, 2010)

The flux-flux correlation function formalism is a standard and widely used approach for the computation of reaction rates. In this paper we introduce a method to compute the classical and quantum flux-flux correlation functions for anharmonic barriers essentially analytically through the use of the classical and quantum normal forms. In the quantum case we show that the quantum normal form reduces the computation of the flux-flux correlation function to that of an effective one dimensional anharmonic barrier. The example of the computation of the quantum flux-flux correlation function for a fourth order anharmonic barrier is worked out in detail, and we present an analytical expression for the quantum mechanical microcanonical flux-flux correlation function. We then give a discussion of the short-time and harmonic limits.

PACS numbers: 02., 05., 34.10.+x, 34.50.Lf, 82.20.-w, 82.20.Db

I. INTRODUCTION

In spite of the tremendous increase in computer power over the last decades, the computation of quantum reaction rates still is a formidable task. This is the topic of this paper, and we begin by giving the setting that is relevant to our work.

The microcanonical rate constant is given by

$$k(E) = (2\pi\hbar\rho_r(E))^{-1}N(E), \quad (1)$$

where $\rho_r(E)$ is the density of states of reactants and $N(E)$ is the cumulative reaction probability, which in turn can be formally expressed in terms of the \mathbf{S} matrix as

$$N(E) = \sum_J (2J+1) \sum_{n_p, n_r} |S_{n_p, n_r}(E, J)|^2. \quad (2)$$

Here the inner sum runs over the asymptotic states of reactants and products which are labeled by n_r and n_p , respectively, and the outer sum covers all values of total angular momentum J .

Though formally correct, the computation of a reaction rate via the \mathbf{S} matrix is extremely inefficient since the computationally expensive information related to the state-to-state reactivities embodied in the \mathbf{S} matrix is "thrown away" as a consequence of the averaging embodied in the summations in (2). Motivated by the success of transition state theory (TST) for computing reaction rates using classical mechanics, many researchers have sought a quantum mechanical version of transition state theory. Recall that the main idea of TST as invented by Eyring, Polanyi and Wigner in the 1930s is to compute classical reaction rates from the flux through a dividing surface in phase space which separates the phase space region associated with reactants from the phase space region associated with products. Assuming the dividing surface to be given by an equation $s(\mathbf{z}) = 0$, where s is a scalar function on the $2f$ -dimensional phase space

with coordinates $\mathbf{z} = (\mathbf{q}, \mathbf{p}) = (q_1, \dots, q_f, p_1, \dots, p_f)$ with $s(\mathbf{z}) < 0$ in the reactants region and $s(\mathbf{z}) > 0$ in the products region, the classical microcanonical rate constant can be written as

$$k_{\text{CL}}(E) = \rho_r(E)^{-1} (2\pi\hbar)^{-f} \int d\mathbf{z} \delta(E - H(\mathbf{z})) F(\mathbf{z}). \quad (3)$$

Here $F(\mathbf{z})$ is the so called flux factor which is given by

$$F(\mathbf{z}) = \left. \frac{d}{dt} \Theta(s(\mathbf{z}_t)) \right|_{t=0} = -\{H, \Theta(s)\}(\mathbf{z}) \quad (4)$$

with Θ denoting the Heaviside function, $\{\cdot, \cdot\}$ denoting the Poisson bracket and \mathbf{z}_t denoting the solution of Hamilton's equations at time t with initial conditions $\mathbf{z}_0 = \mathbf{z}$, i.e. $\mathbf{z}_t = \Phi_H^t(\mathbf{z})$, where Φ_H is the Hamiltonian flow which acts on \mathbf{z} for time t .

For the TST computation of the rate constant to be useful the dividing surface needs to have the property that it is crossed exactly once by reactive trajectories (i.e. trajectories evolving from reactants to products) and not crossed at all by nonreactive trajectories. A dividing surface not satisfying this no-recrossing property leads to an overestimation of the reaction rate. The construction of a recrossing free dividing surface has posed a major problem in the development of TST. Formally, recrossing trajectories are eliminated by multiplying the integrand in (3) by the projection function

$$P_r(\mathbf{z}) = \lim_{t \rightarrow +\infty} \Theta(s(\mathbf{z}_t)) \quad (5)$$

which evaluates to 1 if the trajectory $\mathbf{z}_t = \Phi_H^t(\mathbf{z})$ evolves to products for $t \rightarrow +\infty$, and to 0 otherwise. It is then not difficult to see that the this way corrected expression for the rate constant can be written in the form

$$k_{\text{CL}}(E) = (2\rho_r(E))^{-1} \int_{-\infty}^{\infty} dt \mathcal{C}_{\text{CL}}(E, t), \quad (6)$$

where $\mathcal{C}_{\text{CL}}(E, t)$ is the flux-flux correlation function (FFCF)

$$\mathcal{C}_{\text{CL}}(E, t) = (2\pi\hbar)^{-f} \int d\mathbf{z} \delta(E - H(\mathbf{z})) F(\mathbf{z}) F(\mathbf{z}_t). \quad (7)$$

The canonical analogues of the microcanonical expression above are easily obtained from replacing the density of states $\delta(E - H(\mathbf{z}))$ by its canonical counterpart $\exp(-\beta H(\mathbf{z}))$ ($\beta = (k_{\text{B}}T)^{-1}$ denoting the inverse temperature). Miller, Schwartz and Tromp [1] and Yamamoto [2] took this as a starting point to express the quantum mechanical rate constant in a similar fashion. For the microcanonical case, this amounts to replacing the phase space functions above by the corresponding operators and the integrals over phase space by the traces of operators. For the quantum analogue of the rate constant in (3), this leads to

$$k_{\text{QM}}(E) = \rho_{\text{r}}(E)^{-1} \text{Tr} \left\{ \delta(E - \hat{H}) \hat{F} \hat{P}_{\text{r}} \right\}, \quad (8)$$

where $\rho_{\text{r}}(E)$ now is the quantum mechanical partition function of the reactants (for which we use the same symbol as in the classical case), the flux factor (4) becomes the operator

$$\hat{F} = \frac{d}{dt} \left(e^{i\hat{H}t/\hbar} \Theta(\hat{s}) e^{-i\hat{H}t/\hbar} \right) \Big|_{t=0} = \frac{i}{\hbar} [\hat{H}, \Theta(\hat{s})] \quad (9)$$

and the projection function (5) becomes the operator

$$\hat{P}_{\text{r}} = \lim_{t \rightarrow +\infty} e^{i\hat{H}t/\hbar} \Theta(\hat{s}) e^{-i\hat{H}t/\hbar}. \quad (10)$$

Similarly to the classical case expression (8) for the quantum rate constant can then also be rewritten in terms of a flux-flux correlation function, namely

$$k_{\text{QM}}(E) = (2\rho_{\text{r}}(E))^{-1} \int_{-\infty}^{\infty} dt \mathcal{C}_{\text{QM}}(E, t) \quad (11)$$

with

$$\mathcal{C}_{\text{QM}}(E, t) = \text{Tr} \left\{ \delta(E - \hat{H}) \hat{F} e^{i\hat{H}t/\hbar} \hat{F} e^{-i\hat{H}t/\hbar} \right\}. \quad (12)$$

Clearly, the ability to compute the quantum mechanical flux-flux correlation function is essential for computing quantum mechanical reaction rates using this approach. Exact expressions for the *canonical* quantum mechanical flux-flux correlation function can be found in [1] for the free particle and in [1, 3, 4] for the one degree-of-freedom (quadratic) parabolic barrier. Calculations for other one degree-of-freedom systems have also been carried out numerically. In particular, the quantum mechanical flux-flux correlation functions for the symmetric and asymmetric Eckart and the double-well potential have been studied in detail (see [5, 6]). However, these computations were no *ab initio* computations leading to analytical expressions, but were carried out using various computational techniques. Indeed, the development of

computational techniques to compute the quantum mechanical flux-flux correlation function has been a subject of great interest since the development of this approach.

The traditional approach of quantum mechanics involves basis function techniques, and a review of this approach is given in [7, 8]. While this particular computational approach has proven successful for “moderately” sized molecules, difficulties are encountered when “large” systems (such as biomolecules) are considered. The obstacle has been termed the “exponential wall” of difficulty that one encounters when attempting to perform numerical quantum calculations in the traditional manner for many degree of freedom systems [9]. Semiclassical methods provide an alternative approach. They have been pioneered by Miller and provide significant computational advantages for “large” systems; see [10] for a recent review.

In this paper we present a third approach based on recent work on the phase space approach to quantum mechanics that relies heavily on the dynamical systems framework arising from the application of classical and quantum normal form theory. Classically, this approach has provided a way of constructing a recrossing free dividing surface in the neighborhood of a saddle type equilibrium point which forms the barrier between reactants and products (more precisely the existence of the recrossing free dividing surface is guaranteed for energies not too far away from the energy of the saddle) [11–14]. The dividing surface at a given energy is bounded by a so called *normally hyperbolic invariant manifold* (NHIM) [15] which as an invariant subsystem with the given energy forms a ‘supermolecule’ localized between reactants and products which can be viewed as the transition state that gave TST its name. The dividing surface and the NHIM can be constructed in an algorithmic fashion based on a *classical normal form* (CNF) which can be computed in the neighborhood of the saddle. This is a nonlinear canonical transformation of the phase space coordinates which, to any desired order, decouples the dynamics near the saddle into a single reactive mode and bath modes. (Note: the “decoupling” occurs through a local integrable approximation valid in a neighborhood of the saddle, and does in general *not* imply separability.) More recently it has been shown that the classical construction can be generalized to the quantum case [16–18]. This essentially involves a systematic quantization of the canonical transformation leading to the decoupling in the classical case. The result is a so called *quantum normal form* (QNF) which leads to a local decoupling also of the quantum dynamics into a reactive mode and bath modes.

The main objective of this paper is to use the classical and quantum normal forms to analytically compute the classical and quantum FFCFs for anharmonic barriers. The outline is as follows. In Sec. II we describe how the classical and quantum normal forms can be used to express the classical and quantum mechanical FFCFs. Sec. II A is concerned with the classical case, and we show how the dividing surface having the no-recrossing

property obtained from classical normal form theory enables a computation of the FFCE that does not require the computation of trajectories. Sec. II B is concerned with the quantum case and we show how the quantum normal form approach enables a reduction of the computation of the FFCE in the general f degree-of-freedom case to the case of a one degree-of-freedom anharmonic barrier. Then in Sec. III we work out in detail the micro-canonical quantum FFCE for the example of a barrier in one dimension described by a fourth order anharmonic barrier.

By itself this result should be of some interest because it is the first explicit example of an exact calculation of the FFCE for an anharmonic potential. In Sec. IV we give a discussion of our results and an outlook for future work. The technicalities of two computations are deferred to appendices.

II. THE FLUX-FLUX CORRELATION FUNCTION IN THE FRAMEWORK OF CLASSICAL AND QUANTUM NORMAL FORM THEORY

We begin by showing how classical and quantum normal form theory can be used to calculate both the classical and quantum FFCE for reactions associated with barrier given by an index one saddle of the potential energy surface. In fact the (slightly more general) starting point is an equilibrium point of Hamilton's equations which is of saddle-center-....-center stability type. For a system with f degrees-of-freedom, this means that the matrix associated with the linearization of Hamilton's equations about the equilibrium point has one pair of real eigenvalues $\pm\lambda$ and $f - 1$ complex conjugate pairs of imaginary eigenvalues $\pm i\omega_k$, $k = 2, \dots, f$. We will call such an equilibrium point a saddle for short. For simplicity, we will restrict ourselves to the generic situation where the linear frequencies ω_k are not resonant, i.e. $m_2\omega_1 + \dots + m_f\omega_f \neq 0$ for every nonzero vector of integers (m_2, \dots, m_f) .

A. The classical case

Classical normal form (CNF) theory [12, 17, 18] provides an algorithm for constructing a (nonlinear) canonical transformation $\mathbf{z} \mapsto \mathbf{Z} = (Q_1, \dots, Q_f, P_1, \dots, P_f)$ which, after truncation at a suitable order N , leads to an integrable approximation of the dynamics near the saddle. In terms of the normal form coordinates \mathbf{Z} the N th order CNF of the original Hamilton function $H(\mathbf{z})$ assumes the following form

$$\begin{aligned} H_{\text{CNF}}^{(N)}(\mathbf{Z}) &= K_{\text{CNF}}^{(N)}(I, J_2, J_3, \dots, J_f) \\ &= \sum_{n=0}^{\lfloor N/2 \rfloor} \sum_{|\alpha|=n} \kappa_{n,\alpha} I^{\alpha_1} J_2^{\alpha_2} \dots J_f^{\alpha_f}. \end{aligned} \quad (13)$$

Here $\lfloor \cdot \rfloor$ denotes the floor function, the $\alpha = (\alpha_1, \dots, \alpha_f)$ are vectors with nonnegative integer components and norm $|\alpha| = \sum_{k=1}^f \alpha_k$,

$$I = \frac{1}{2} (P_1^2 - Q_1^2) \quad (14)$$

is an action type integral associated with the reactive mode, and

$$J_k = \frac{1}{2} (P_k^2 + Q_k^2), \quad k = 2, \dots, f, \quad (15)$$

are action integrals of the bath modes which we group together in the vector \mathbf{J} . The CNF transformation (including the coefficients $\kappa_{n,\alpha}$ in (13)) can be computed in an algorithmic fashion as described in detail in [17].

In terms of the normal form coordinates the dividing surface is given by $s(\mathbf{Z}) = Q_1$. Then, following the definition in Eq. (4) the flux factor is given by

$$\begin{aligned} F(\mathbf{Z}) &= \left. \frac{d}{dt} \Theta(Q_{1t}) \right|_{t=0} = - \left\{ H_{\text{CNF}}^{(N)}, \Theta(Q_1) \right\}(\mathbf{Z}) \\ &= \delta(Q_1) \nu(I, \mathbf{J}) P_1, \end{aligned} \quad (16)$$

where

$$\nu(I, \mathbf{J}) = \frac{\partial}{\partial I} K_{\text{CNF}}^{(N)}(I, \mathbf{J}). \quad (17)$$

Following (7) the FFCE then takes the form

$$\begin{aligned} \mathcal{C}_{\text{CL}}(E, t) &= \int d\mathbf{Z} \delta(E - H_{\text{CNF}}^{(N)}(\mathbf{Z})) \\ &\quad \times \delta(Q_1) \delta(Q_{1t}) \nu^2(I, \mathbf{J}) P_1 P_{1t}. \end{aligned} \quad (18)$$

The product of the δ -functions of Q_1 and the corresponding time evolved coordinate Q_{1t} (using the flow associated with $H_{\text{CNF}}^{(N)}$) indicates that only the infinitesimally short time scales $t \rightarrow 0$ give a non-vanishing contribution to the integral. The short-time expansion $Q_{1t} = Q_1 + \nu(I, \mathbf{J}) P_1 t + \mathcal{O}(t^2)$ and $P_{1t} = P_1 + \mathcal{O}(t)$ yields

$$\mathcal{C}_{\text{CL}}(E, t) = 2f(E) \delta(t), \quad (19)$$

where

$$\begin{aligned} f(E) &= \frac{1}{2} \int d\mathbf{Z} \delta(E - H_{\text{CNF}}^{(N)}(\mathbf{Z})) \delta(Q_1) \nu(I, \mathbf{J}) |P_1| \\ &= (2\pi)^{f-1} \int_{\mathbb{R}_+^f} dI d\mathbf{J} \delta(E - K_{\text{CNF}}^{(N)}(I, \mathbf{J})) \nu(I, \mathbf{J}) \\ &= (2\pi)^{f-1} \int_{I(E, \mathbf{J}) > 0} d\mathbf{J}, \end{aligned} \quad (20)$$

with $I = I(E, \mathbf{J})$ solving the energy equation $H_{\text{CNF}}^{(N)}(I, \mathbf{J}) = E$. The last integral in Eq. (20) is the volume in the space of the center actions $\mathbf{J} = (J_2, \dots, J_f)$ enclosed by the contour $H_{\text{CNF}}^{(N)}(0, \mathbf{J}) = E$, and accordingly $f(E)$ is nothing but the directional flux through the dividing surface [17, 18].

We note that formally the result given by Eq. (19) exists in the literature before (e.g., see Refs. [8, 19] for a corresponding canonical version of the formula). However, the contribution of the classical normal form theory in providing a dividing surface with the no-recrossing property provides a new formula, and interpretation, of the pre-factor $f(E)$ in terms of an integral, in the bath mode action space, over the NHIM. This eliminates the need to compute trajectories (and the projection function (5)) in the computation of the classical FFCF.

B. The quantum mechanical case

In [16–18] a quantum normal form (QNF) procedure has been developed that yields a local decoupling of a reactive mode and the bath modes also in the quantum mechanical case if the corresponding classical system has a saddle equilibrium of the form described above. In the quantum case the local simplification of the Hamilton operator is achieved by conjugating it with a suitable unitary transformation. Similar to the classical case this unitary transformation and the transformed Hamilton operator can be computed in an algorithmic fashion. The transformed operator then takes the form of a power series in terms of elementary operators associated with the reactive and bath modes and, in addition, Planck's constant. Truncating this expansion at a suitable order N gives the N th order QNF approximation $\hat{H}_{\text{QNF}}^{(N)}$ which is of the form

$$\begin{aligned} \hat{H}_{\text{QNF}}^{(N)} &= K_{\text{QNF}}^{(N)}(\hat{I}, \hat{J}_2, \hat{J}_3, \dots, \hat{J}_f) \\ &= \sum_{n=0}^{[N/2]} \sum_{|\alpha|+j=n} \kappa_{n,\alpha,j} \hat{I}^{\alpha_1} \hat{J}_2^{\alpha_2} \dots \hat{J}_f^{\alpha_f} \hbar^j. \end{aligned} \quad (21)$$

Here, the notation is the same as in (13), where in addition the j are nonnegative integers and

$$\hat{I} = \frac{1}{2} (\hat{P}_1^2 - \hat{Q}_1^2) \quad (22)$$

is an operator associated with the reactive mode, and

$$\hat{J}_k = \frac{1}{2} (\hat{P}_k^2 + \hat{Q}_k^2), \quad k = 2, \dots, f \quad (23)$$

are operators associated with the bath modes. In (22) and (23) the \hat{Q}_k and \hat{P}_k , $k = 1, \dots, f$, are as usual pairs of conjugate position and momentum operators that satisfy the commutation relations $[\hat{Q}_k, \hat{Q}_l] = [\hat{P}_k, \hat{P}_l] = 0$ and $[\hat{Q}_k, \hat{P}_l] = i\hbar \delta_{kl}$. The approximation of the original Hamilton operator by the QNF in Eq. (21) holds locally in the vicinity of the saddle equilibrium of the corresponding classical system in a sense that is made precise in [17].

Since the trace of an operator is invariant under unitary conjugations of the operator we can evaluate

Eq. (12) using the QNF to get

$$\begin{aligned} \mathcal{C}_{\text{QM}}(E, t) &= \text{Tr} \left\{ \delta \left(E - \hat{H}_{\text{QNF}}^{(N)} \right) \hat{F}_{\text{QNF}}^{(N)} e^{i\hat{H}_{\text{QNF}}^{(N)} t/\hbar} \hat{F}_{\text{QNF}}^{(N)} e^{-i\hat{H}_{\text{QNF}}^{(N)} t/\hbar} \right\} \end{aligned} \quad (24)$$

with the flux operator given by

$$\hat{F}_{\text{QNF}}^{(N)} = \frac{i}{\hbar} [\hat{H}_{\text{QNF}}^{(N)}, \Theta(\hat{Q}_1)]. \quad (25)$$

Since the operators \hat{I} and \hat{J}_k , $k = 2, \dots, f$, mutually commute the eigenstates of $\hat{H}_{\text{QNF}}^{(N)}$ can be chosen such that they are simultaneously the eigenstates of all the elementary operators \hat{I} and \hat{J}_k , whose spectral properties are well known. Thus,

$$\hat{H}_{\text{QNF}}^{(N)} |I, n_2, \dots, n_f\rangle = E |I, n_2, \dots, n_f\rangle \quad (26)$$

with

$$|I, n_2, \dots, n_f\rangle = |\psi_I\rangle \otimes |\psi_{n_2}\rangle \otimes \dots \otimes |\psi_{n_f}\rangle, \quad (27)$$

where

$$\hat{I} |\psi_I\rangle = I |\psi_I\rangle, \quad I \in \mathbb{R}, \quad (28a)$$

$$\hat{J}_k |\psi_{n_k}\rangle = \hbar(n_k + 1/2) |\psi_{n_k}\rangle, \quad n_k \in \mathbb{N}_0, \quad (28b)$$

and

$$E = K_{\text{QNF}}^{(N)}(I, \hbar(n_2 + 1/2), \dots, \hbar(n_f + 1/2)). \quad (29)$$

Using the basis given by the eigenstates $|I, n_2, \dots, n_f\rangle$ one can now straightforwardly trace out the bath modes in Eq. (24). Indeed, let us define the operator

$$\begin{aligned} \hat{\mathcal{H}}_{n_2, \dots, n_f}^{(N)} &= \sum_{n=0}^{[N/2]} \sum_{|\alpha|+j=n} \kappa_{n,\alpha,j} \hat{I}^{\alpha_1} \\ &\times \left(n_2 + \frac{1}{2} \right)^{\alpha_2} \dots \left(n_f + \frac{1}{2} \right)^{\alpha_f} \hbar^{|\alpha| - \alpha_1 + j} \end{aligned} \quad (30)$$

parametrized by the $(f-1)$ nonnegative quantum numbers n_2, \dots, n_f . Then Eqs (24) and (25) can be written as

$$\mathcal{C}_{\text{QM}}(E, t) = \sum_{n_2, \dots, n_f} \text{Tr} \left\{ \delta(E - \hat{\mathcal{H}}) \hat{\mathcal{F}} e^{i\hat{\mathcal{H}}t/\hbar} \hat{\mathcal{F}} e^{-i\hat{\mathcal{H}}t/\hbar} \right\} \quad (31)$$

and

$$\hat{\mathcal{F}} = \frac{i}{\hbar} [\hat{\mathcal{H}}, \Theta(\hat{Q}_1)] \quad (32)$$

respectively, where, to avoid a cumbersome notation, we have dropped the superscript N and subscripts n_2, \dots, n_f for the operators $\hat{\mathcal{H}}$ and $\hat{\mathcal{F}}$.

Equations (31) and (32) show that the problem of calculating the quantum FFCF for a system with $f > 1$

degrees of freedom effectively reduces to the corresponding problem for a one-dimensional system described by a Hamiltonian of the form Eq. (30) which is a polynomial of the operator \hat{I} associated with the reactive mode only. In the following section we present an explicit calculation of the FFCF for the simplest *anharmonic* one-dimensional Hamiltonian of this form.

III. THE QUANTUM FLUX-FLUX CORRELATION FUNCTION FOR ONE DIMENSIONAL ANHARMONIC BARRIERS

We now present an analytical calculation of the FFCF for the two-parameter family of Hamilton operators defined by

$$\hat{H}(a, \lambda) = \hat{h} + a\hat{h}^2, \quad \hat{h} = \frac{1}{2}(\hat{p}^2 - \lambda^2\hat{q}^2). \quad (33)$$

Here λ parametrizes the width of the barrier in the harmonic approximation and a characterizes the anharmonicity of the barrier. The Hamiltonian operator \hat{H} can be viewed to be in quantum normal form. In fact the operator \hat{h} differs from the operator \hat{I} defined in Sec. II B only by a factor of λ which follows from a linear transformation of \hat{p} and \hat{q} which does not alter the normal form procedure described in the previous section. The Hamilton operator in (33) can therefore be considered to describe the simplest possible anharmonic barrier.

The starting point of our calculation is the system of eigenstates of \hat{h} , (and therefore of \hat{H})

$$\hat{h}|\psi_\sigma^E\rangle = E|\psi_\sigma^E\rangle, \quad E \in \mathbb{R}, \quad \sigma = \pm 1. \quad (34)$$

The corresponding wavefunctions are [20, 21]

$$\begin{aligned} \langle q|\psi_\sigma^E\rangle &= \frac{1}{2\pi\hbar} \left(\frac{2\hbar}{\lambda}\right)^{\frac{1}{4}} \exp\left(\frac{\pi E}{4\lambda\hbar}\right) \Gamma\left(\frac{1}{2} - i\frac{E}{\lambda\hbar}\right) \\ &\times D_{-\frac{1}{2} + i\frac{E}{\lambda\hbar}}\left(\sigma e^{-i\frac{\pi}{4}} \sqrt{\frac{2\lambda}{\hbar}} q\right), \end{aligned} \quad (35)$$

where D_ν denotes the parabolic cylinder function of order ν [22]. The eigenstates are mutually orthogonal,

$$\langle \psi_\sigma^E | \psi_{\sigma'}^{E'} \rangle = \delta_{\sigma, \sigma'} \delta(E - E'), \quad (36)$$

and form a complete basis, i.e.,

$$\sum_{\sigma=\pm 1} \int_{-\infty}^{+\infty} dE |\psi_\sigma^E\rangle \langle \psi_\sigma^E| = \hat{\mathbf{1}}, \quad (37)$$

where $\hat{\mathbf{1}}$ denotes the identity operator.

Using the $|\psi_\sigma^E\rangle$ basis to expand the trace in Eq. (31) we can write the quantum FFCF as

$$\begin{aligned} \mathcal{C}_{\text{QM}}(E, t, a) &= \iint dE' dE'' \delta(E'' + aE''^2 - E) \\ &\times \exp\left[\frac{it}{\hbar}(E' + aE'^2 - E)\right] \sum_{\sigma, \sigma'} \left| \langle \psi_\sigma^{E''} | \hat{F} | \psi_{\sigma'}^{E'} \rangle \right|^2, \end{aligned} \quad (38)$$

where for the discussion below, we explicitly added the anharmonicity parameter a to the argument of the FFCF (note that as opposed to a the parameter λ can in principle be removed by a suitable scaling of the energy). If we denote the two solutions of $\tilde{E} + a\tilde{E}^2 = E$ by

$$\tilde{E}_\sigma = \frac{1}{2a} \left(-1 + \sigma\sqrt{1 + 4aE}\right), \quad \sigma = \pm 1, \quad (39)$$

then (38) becomes

$$\begin{aligned} \mathcal{C}_{\text{QM}}(E, t, a) &= \frac{1}{\sqrt{1 + 4aE}} \int_{-\infty}^{+\infty} dE' e^{i(E' + aE'^2 - E)t/\hbar} \\ &\times \sum_{\sigma, \sigma', \sigma''} \left| \langle \psi_\sigma^{\tilde{E}_{\sigma''}} | \hat{F} | \psi_{\sigma'}^{E'} \rangle \right|^2 \end{aligned} \quad (40)$$

if $1 + 4aE > 0$, and $\mathcal{C}_{\text{QM}}(E, t, a) = 0$ else. The latter condition on the energy E and the parameter a simply assures that we actually have a barrier scattering problem if the inequality is satisfied.

The matrix elements of the flux operator \hat{F} are calculated as follows. According to Eq. (32) we have

$$\hat{F} = \frac{i}{\hbar} [\hat{h} + a\hat{h}^2, \Theta(\hat{q})], \quad (41)$$

so that

$$\begin{aligned} \langle \psi_\sigma^E | \hat{F} | \psi_{\sigma'}^{E'} \rangle &= \frac{i}{\hbar} [(E + aE^2) - (E' + aE'^2)] \\ &\times \int_0^\infty dq \langle \psi_\sigma^E | q \rangle \langle q | \psi_{\sigma'}^{E'} \rangle. \end{aligned} \quad (42)$$

Then, using Eq. (35) into Eq. (42) and performing the integration over q we obtain

$$\begin{aligned} \langle \psi_\sigma^E | \hat{F} | \psi_{\sigma'}^{E'} \rangle &= \frac{1 + a(E + E')}{8\pi^2\hbar} e^{\frac{\pi}{4} \frac{E+E'}{\lambda\hbar}} 2^{\frac{1}{2}} \frac{E-E'}{\lambda\hbar} \\ &\times \left\{ \sigma e^{-i\frac{\pi}{4}} \Gamma\left(\frac{3}{4} + i\frac{E}{2\lambda\hbar}\right) \Gamma\left(\frac{1}{4} - i\frac{E'}{2\lambda\hbar}\right) \right. \\ &\left. + \sigma' e^{i\frac{\pi}{4}} \Gamma\left(\frac{1}{4} + i\frac{E}{2\lambda\hbar}\right) \Gamma\left(\frac{3}{4} - i\frac{E'}{2\lambda\hbar}\right) \right\}. \end{aligned} \quad (43)$$

This finally leads to the following expression for the double sum (over σ and σ') entering Eqs. (38) and (40):

$$\begin{aligned} \sum_{\sigma, \sigma'} \left| \langle \psi_\sigma^E | \hat{F} | \psi_{\sigma'}^{E'} \rangle \right|^2 &= \frac{[1 + a(E + E')]^2}{16\pi^4\hbar^2} \exp\left(\frac{\pi E + E'}{2\lambda\hbar}\right) \\ &\times \left\{ \left| \Gamma\left(\frac{1}{4} + i\frac{E}{2\lambda\hbar}\right) \right|^2 \left| \Gamma\left(\frac{3}{4} + i\frac{E'}{2\lambda\hbar}\right) \right|^2 \right. \\ &\left. + \left| \Gamma\left(\frac{3}{4} + i\frac{E}{2\lambda\hbar}\right) \right|^2 \left| \Gamma\left(\frac{1}{4} + i\frac{E'}{2\lambda\hbar}\right) \right|^2 \right\}. \end{aligned} \quad (44)$$

We then substitute Eq. (44) into Eq. (40) and use the

formula (see Appendix A for its derivation)

$$\begin{aligned} & \int_{-\infty}^{+\infty} dx e^{iAx^2+Bx} (1+Cx)^2 |\Gamma(D+ix)|^2 \\ &= 2\pi \frac{\Gamma(2D)}{2^{2D}} \exp\left(-i\frac{A}{4}\frac{\partial^2}{\partial x^2}\right) \\ & \quad \frac{(\cosh x + iCD \sinh x)^2 + \frac{1}{2}C^2D}{(\cosh x)^{2D+2}} \Bigg|_{x=-i\frac{B}{2}} \end{aligned} \quad (45)$$

with $A = 4a\lambda^2\hbar t$, $B = \pi + 2i\lambda t$, $C = 2\lambda ta/(1 + a\tilde{E})$, and $D = 1/4$ or $3/4$ to arrive at the central result of our paper:

$$C_{\text{QM}}(E, t, a) = \frac{\lambda e^{i\pi/4}}{2^{9/2}\pi^{5/2}\hbar} \Lambda(E/\lambda\hbar, \lambda t, a\lambda\hbar), \quad (46a)$$

where

$$\begin{aligned} \Lambda(\varepsilon, \tau, \alpha) &= \frac{e^{-i\varepsilon\tau}}{\sqrt{1+4\varepsilon\alpha}} \sum_{\sigma=\pm 1} \exp\left(\frac{\pi\varepsilon\sigma}{2}\right) \left\{ \right. \\ & \quad 4 \left| \Gamma\left(\frac{3}{4} + i\frac{\varepsilon\sigma}{2}\right) \right|^2 \Omega_{-\sigma}\left(\frac{1}{4}; \varepsilon, \tau, \alpha\right) \\ & \quad \left. + i \left| \Gamma\left(\frac{1}{4} + i\frac{\varepsilon\sigma}{2}\right) \right|^2 \Omega_{-\sigma}\left(\frac{3}{4}; \varepsilon, \tau, \alpha\right) \right\}, \end{aligned} \quad (46b)$$

$$\varepsilon_{\sigma}(\varepsilon, \alpha) = \frac{1}{2\alpha} (-1 + \sigma\sqrt{1+4\varepsilon\alpha}), \quad (46c)$$

and

$$\begin{aligned} \Omega_{\sigma}(\nu; \varepsilon, \tau, \alpha) &= \alpha^2 \exp\left(-i\alpha\tau\frac{\partial^2}{\partial\tau^2}\right) \frac{(\varepsilon_{\sigma} \sinh \tau - 2i\nu \cosh \tau)^2 - 2\nu}{(\sinh \tau)^{2\nu+2}}. \end{aligned} \quad (46d)$$

The expression for the FFCF given by Eq. (46) is *exact* and holds for all energies E and parameters a satisfying $1 + 4aE > 0$. (As shown above, $C_{\text{QM}}(E, t, a) = 0$ if $1 + 4aE < 0$.) In the following we consider the limits of an harmonic saddle, $a \rightarrow 0$, and short times $\lambda t \ll 1$ for which cases Ω_{σ} in Eq. (46d) assumes a simpler form.

A. The case of a harmonic barrier ($a = 0$)

In the limit $\alpha \rightarrow 0$ Eq. (46c) yields $\varepsilon_1 = \varepsilon + \mathcal{O}(\alpha)$ and $\varepsilon_{-1} = -1/\alpha - \varepsilon + \mathcal{O}(\alpha)$. It is then straightforward to show that for $\alpha = 0$ the $\sigma = -1$ contribution to the sum in the right-hand side of Eq. (46b) vanishes and thus

$$\Lambda(\varepsilon, \tau, 0) = e^{\varepsilon(\frac{\pi}{2}-i\tau)} \left[4 \frac{|\Gamma(\frac{3}{4} + \frac{i\varepsilon}{2})|^2}{(\sinh \tau)^{1/2}} + i \frac{|\Gamma(\frac{1}{4} + \frac{i\varepsilon}{2})|^2}{(\sinh \tau)^{3/2}} \right], \quad (47)$$

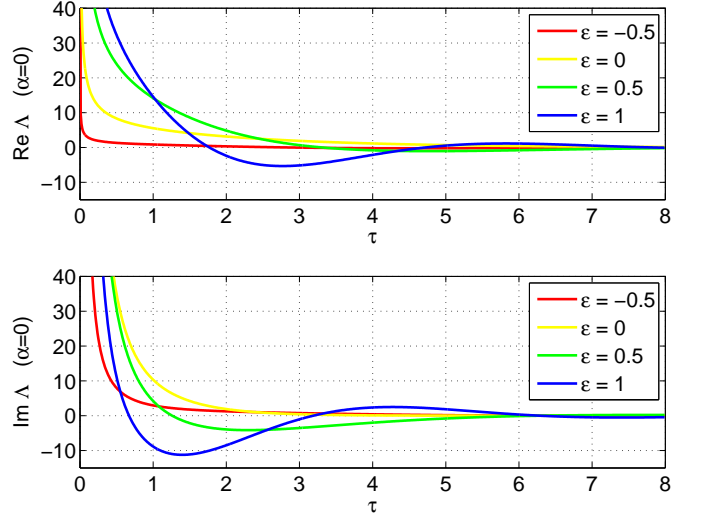


FIG. 1: (Color online) The time dependence of the real (top) and imaginary (bottom) parts of the function Λ in (47) which enters the quantum FFCF for an harmonic barrier in (46a). The graphs are for different values of the scaled energy ε .

which is valid for all energies, $\varepsilon \in \mathbb{R}$.

Equations (46a) and (47) yield an exact expression for the *microcanonical* quantum FFCF of the parabolic barrier system with Hamiltonian $(\hat{p}^2 - \lambda^2 \hat{q}^2)/2$. The corresponding *canonical* version of the FFCF, defined as

$$\bar{C}_{\text{QM}}(\beta, t, a) = \text{Tr} \left\{ e^{-\beta\hat{H}} \hat{F} e^{i\hat{H}t/\hbar} \hat{F} e^{-i\hat{H}t/\hbar} \right\}, \quad (48)$$

can be readily calculated for the case of $a = 0$ by performing the bilateral Laplace transformation of (46a) which gives

$$\begin{aligned} \bar{C}_{\text{QM}}(\beta, t, 0) &= \int_{-\infty}^{+\infty} dE e^{-\beta E} C_{\text{QM}}(E, t, 0) \\ &= \frac{\lambda^2}{4\pi} \frac{\cosh(\lambda t_c) \sinh(\lambda\hbar\beta/2)}{[\sinh^2(\lambda t_c) + \cosh^2(\lambda\hbar\beta/2)]^{3/2}} \end{aligned} \quad (49)$$

with $t_c = t - i\hbar\beta/2$. Here Eq. (45) with $A = C = 0$ was used to calculate the integral over energy.

We note that Eq. (49) was originally obtained by Miller *et al.* [1] by representing the FFCF in terms of the time evolution operator for the harmonic oscillator. However, to our knowledge, the explicit expression for the microcanonical FFCF in Eqs. (46a) and (47) has not been reported in the literature before.

In Fig. 1 the time dependence of the function Λ in (47) is shown for different values of the scaled energy ε . We note that Λ and hence the microcanonical FFCF always diverge in the limit $t \rightarrow 0$ and depending on the energy shows more or less pronounced oscillations.

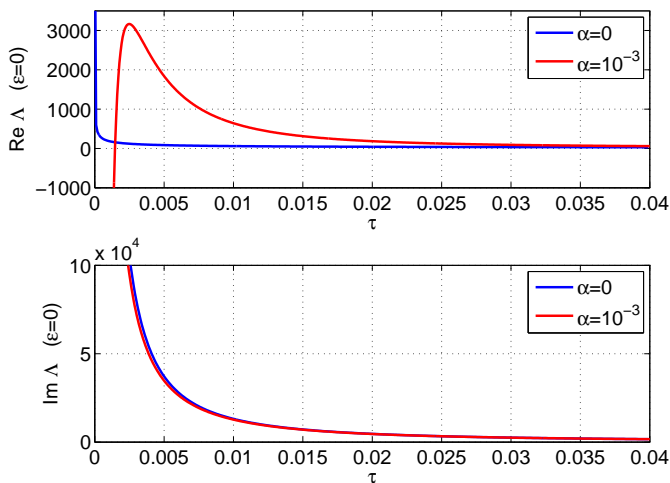


FIG. 2: (Color online) Short time regime of the real (top) and imaginary (bottom) parts of the function Λ which enters the quantum FFCF in (46a) (see Sec. III B). The graphs are for different values of the scaled anharmonicity parameter α and all have energy zero.

B. The short-time regime ($\lambda t \ll 1$)

For short times, $\tau \ll 1$, one can approximate the hyperbolic functions on the right-hand side of Eq. (46d) by their leading order Taylor expansions to obtain

$$\begin{aligned} \Omega_\sigma(\nu; \varepsilon, \tau, \alpha) \\ \simeq \alpha^2 (\varepsilon_\sigma^2 \mathcal{D}_{2\nu} - 4i\nu\varepsilon_\sigma \mathcal{D}_{2\nu+1} + 2\nu(2\nu+1)\mathcal{D}_{2\nu+2}) \end{aligned} \quad (50)$$

with

$$\mathcal{D}_\mu(\tau, \alpha) = \exp\left(-i\alpha\tau \frac{\partial^2}{\partial \tau^2}\right) \frac{1}{\tau^\mu}. \quad (51)$$

As shown in Appendix B \mathcal{D}_μ in Eq. (51) can be written as

$$\mathcal{D}_\mu(\tau, \alpha) = e^{\gamma^2/4} D_{-\mu}(\gamma) \left(\frac{\gamma}{\tau}\right)^\mu, \quad \gamma = \left(\frac{\tau}{2\alpha} e^{-i\pi/2}\right)^{1/2}. \quad (52)$$

Equations (46a-46c) together with Eqs. (50) and (52) provide an explicit expression for the FFCF at short times.

Figure 2 compares the time decay of the dimensionless correlation function Λ in the harmonic case ($\alpha = 0$, blue lines), given by Eq. (47), and that in the anharmonic case ($\alpha = 10^{-3}$, red lines), given by Eqs. (46b), (50), and (52). One sees that even for very small (but non-vanishing) values of the dimensionless anharmonicity parameter α the time dependence of the FFCF significantly differs from that of the corresponding harmonic problem. In fact, it is straightforward to show that as $\tau \rightarrow 0$ one has $\text{Re } \Lambda \rightarrow +\infty$ for $\alpha = 0$, while $\text{Re } \Lambda \rightarrow -\infty$ for $\alpha > 0$. The transition from the anharmonic case to the harmonic one takes place in a discontinuous manner:

as α tends to zero the maximum of $\text{Re } \Lambda$ (i.e., the peak of the red curve in the upper half of Fig. 2) becomes higher and sharper and approaches $\tau = 0$ recovering the harmonic result (the monotonic blue curve in Fig. 2).

IV. CONCLUSIONS

In this paper we have presented a method for computing classical and quantum flux-flux correlation functions for reactive systems with a potential barrier characterized by saddle type equilibria in phase space. The method is based on the normal form transformation of the system's Hamiltonian in a vicinity of the saddle point.

In the classical case, the time dependence of the correlation function (with respect to a recrossing free dividing surface) is given by the δ -function. While this form of the time dependence has been known in the theoretical chemistry community for some time, the contribution of the classical normal form theory is that it provides a dividing surface having the no-recrossing property that allows the computation of the pre-factor (essentially the flux through the dividing surface). No computation of trajectories is required to evaluate the flux-flux correlation function. The time integration to compute the rate becomes trivial.

In the quantum case, we showed that the problem of calculating the correlation function in a system with more than one degree-of-freedom reduces to an effective one degree-of-freedom problem. The Hamiltonian of this effective one degree-of-freedom system is obtained through the quantum normal form procedure. Finally, and most importantly, we derive (for the first time in the literature) an analytical expression for the flux-flux correlation function for the simplest *anharmonic* one-dimensional Hamiltonian in quantum normal form.

Acknowledgments

A.G. and H.W. acknowledge support by EPSRC under grant No. EP/E024629/1. S.W. acknowledges the support of the Office of Naval Research Grant No. N00014-01-1-0769.

Appendix A: Derivation of Eq. (45)

We begin our derivation of the formula, Eq. (45), by writing

$$|\Gamma(D + ix)|^2 = \frac{\Gamma(2D)}{2^{2D}} \int_{-\infty}^{+\infty} dq \frac{e^{-iqx}}{[\cosh(q/2)]^{2D}}. \quad (A1)$$

The integral representation given by Eq. (A1) is readily obtained, e.g., from formula 5.13.2 in Ref. [23]. Then,

denoting the left-hand side of Eq. (45) by \mathcal{I} we get

$$\mathcal{I} = \frac{\Gamma(2D)}{2^{2D}} \int_{-\infty}^{+\infty} \frac{dq}{[\cosh(q/2)]^{2D}} \times \int_{-\infty}^{+\infty} dx (1 + Cx)^2 e^{iAx^2 - i(q+iB)x}. \quad (\text{A2})$$

The second integral in the right-hand side of Eq. (A2) can be written as

$$\sum_{n=0}^{\infty} \frac{(iA)^n}{n!} \int_{-\infty}^{+\infty} dx x^{2n} (1 + Cx)^2 e^{-i(q+iB)x}. \quad (\text{A3})$$

Now, using

$$\int_{-\infty}^{+\infty} dx x^n e^{-i(q+iB)x} = 2\pi i^n \delta^{(n)}(q + iB), \quad (\text{A4})$$

with $\delta^{(n)}$ denoting the n th derivative of the delta function, and then, carrying out the q -integration in Eq. (A3) we obtain

$$\mathcal{I} = 2\pi \frac{\Gamma(2D)}{2^{2D}} \sum_{n=0}^{\infty} \frac{(-iA)^n}{n!} \frac{\partial^{2n}}{\partial q^{2n}} \left. \frac{(\cosh \frac{q}{2} + iCD \sinh \frac{q}{2})^2 + \frac{1}{2}C^2D}{(\cosh \frac{q}{2})^{2D+2}} \right|_{q=-iB}. \quad (\text{A5})$$

Finally, formally summing the series,

$$\sum_{n=0}^{\infty} \frac{(-iA)^n}{n!} \frac{\partial^{2n}}{\partial q^{2n}} f(q) = \exp\left(-iA \frac{\partial^2}{\partial q^2}\right) f(q) \quad (\text{A6})$$

with f denoting an arbitrary function, and making the change $x = q/2$ we arrive at Eq. (45).

Appendix B: Derivation of Eq. (52)

Taking into account the identity

$$\frac{1}{\tau^\mu} = \frac{1}{\Gamma(\mu)} \int_0^\infty ds s^{\mu-1} e^{-\tau s} \quad (\text{B1})$$

we rewrite Eq. (51) as

$$\mathcal{D}_\mu = \frac{1}{\Gamma(\mu)} \int_0^\infty ds s^{\mu-1} e^{-i\alpha\tau s^2 - \tau s}. \quad (\text{B2})$$

Then, using formula 3.462.1 in Ref. [24],

$$\int_0^\infty ds s^{\mu-1} e^{-As^2 - Bs} = \frac{\Gamma(\mu)}{(2A)^{\mu/2}} \exp\left(\frac{B^2}{8A}\right) D_{-\mu}\left(\frac{B}{\sqrt{2B}}\right), \quad (\text{B3})$$

for $A = e^{i\pi/2}\alpha\tau$ and $B = \tau$ we arrive at Eq. (52).

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- [1] W. H. Miller, S. D. Schwartz, and J. W. Tromp, *J. Chem. Phys.*, **79**, 4889 (1983).
[2] T. Yamamoto, *J. Chem. Phys.*, **33**, 281 (1960).
[3] W. H. Miller, *J. Chem. Phys.*, **61**, 1823 (1974).
[4] H. Wang, X. Sun, and W. H. Miller, *J. Chem. Phys.*, **108**, 9726 (1998).
[5] M. Ceotto, S. Yang, and W. H. Miller, *J. Chem. Phys.*, **122**, 044109 (2005).
[6] C. Venkataraman and W. H. Miller, *J. Chem. Phys.*, **126**, 094104 (2007).
[7] W. H. Miller, *Farad. Discuss.*, **110**, 1 (1998).
[8] W. H. Miller, *J. Phys. Chem. A*, **102**, 793 (1998).
[9] Department of Energy, "Directing Matter and Energy: Five Challenges for Science and the Imagination. A Report from the Basic Energy Sciences Advisory Committee, US Department of Energy, December 20, 2007," (2007).
[10] W. H. Miller, in *Physical Biology—From Atoms to Cells*, 51st Conference on Chemical Research, edited by K. K. Phua and A. Zewail (Imperial College Press, London, UK, 2008) pp. 505–525.
[11] S. Wiggins, L. Wiesenfeld, C. Jaffe, and T. Uzer, *Phys. Rev. Lett.*, **86**(24), 5478 (2001).
[12] T. Uzer, C. Jaffe, J. Palacian, P. Yanguas, and S. Wiggins, *Nonlinearity*, **15**, 957 (2002).
[13] H. Waalkens, A. Burbanks, and S. Wiggins, *J. Chem. Phys.*, **121**, 6207 (2004).
[14] H. Waalkens and S. Wiggins, *J. Phys. A*, **37**, L435 (2004).
[15] S. Wiggins, *Normally hyperbolic invariant manifolds in dynamical systems* (Springer-Verlag, 1994).
[16] R. Schubert, H. Waalkens, and S. Wiggins, *Phys. Rev. Lett.*, **96**, 218302 (2006).
[17] H. Waalkens, R. Schubert, and S. Wiggins, *Nonlinearity*, **21**, R1 (2008).
[18] A. Goussev, R. Schubert, H. Waalkens, and S. Wiggins, "Quantum theory of reactive scattering in phase space," To appear in *Advances in Quantum Chemistry*, e-print: arXiv:1004.5017.
[19] J. W. Tromp and W. H. Miller, *Faraday Discuss. Chem. Soc.*, **84**, 441 (1987).
[20] D. Chruściński, *J. Math. Phys.*, **44**, 3718 (2003).
[21] D. Chruściński, *J. Math. Phys.*, **45**, 841 (2003).
[22] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables* (Dover, New York, 1965) ISBN 0-486-61272-4.
[23] "Digital library of mathematical functions," National Institute of Standards and Technology,

<http://dlmf.nist.gov/> (2010).

[24] I. S. Gradshteyn and I. M. Ryzhik, *Table of Integrals, Series and Products*, edited by A. Jeffrey and D. Zwillinger

(Academic Press Inc.; 6th edition, 2000).