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The flux-flux correlation function for anharmonic barriers

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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 for a general degree-of-freedom system having an index one saddle 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. © 2010 American Institute of Physics. [doi:10.1063/1.3518425]

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

\[ k(E) = (2\pi\hbar \rho(E))^{-1} N(E), \] (1)

where \( \rho(E) \) 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 \( S \) matrix as

\[ N(E) = \sum_{J} (2J + 1) \sum_{n_p n_r} |S_{n_p n_r}(E, J)|^2. \] (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 \( S \) matrix is extremely inefficient since the computationally expensive information related to the state-to-state reactivities embodied in the \( S \) matrix is “thrown away” as a consequence of the averaging embodied in the summations in Eq. (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 \( s(z) = 0 \), where \( s \) is a scalar function on the \( 2f \)-dimensional phase space with coordinates \( z = (q, p) = (q_1, \ldots, q_f, p_1, \ldots, p_f) \) with \( s(z) < 0 \) in the reactants region and \( s(z) > 0 \) in the products region, the classical microcanonical rate constant can be written as

\[ k_{CL}(E) = \rho(E)^{-1} (2\pi\hbar)^{-f} \int dz \delta(E - H(z)) F(z). \] (3)

Here \( F(z) \) is the so-called flux factor which is given by

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

with \( \Theta \) denoting the Heaviside function, \([\cdot, \cdot]\) denoting the Poisson bracket, and \( z_t \) denoting the solution of Hamilton’s equations at time \( t \) with initial conditions \( z_0 = z \), i.e., \( z_t = \Phi_{H}^t(z) \), where \( \Phi_H^t \) is the Hamiltonian flow which acts on \( z \) 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 Eq. (3) by the projection function

\[ P_t(z) = \lim_{t \to +\infty} \Theta(s(z_t)), \] (5)

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

\[ k_{CL}(E) = (2\rho(E))^{-1} \int_{-\infty}^{+\infty} dt C_{CL}(E, t), \] (6)

where \( C_{CL}(E, t) \) is the flux-flux correlation function (FFCF)

\[ C_{CL}(E, t) = (2\pi\hbar)^{-f} \int dz \delta(E - H(z)) F(z) F(z_t). \] (7)
The canonical analog of the microcanonical expression above are easily obtained from replacing the density of states $\delta(E - H(z))$ by its canonical counterpart $\exp(-\beta H(z))$ ($\beta = (k_B T)^{-1}$ denoting the inverse temperature). Miller, Schwartz, and Tromp, and Yamamoto 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 Eq. (3), this leads to

$$k_{QM}(E) = \rho_0(E)^{-1} \text{Tr} \{ \delta(E - \hat{H}) \hat{F} \hat{F}^\dagger \},$$

where $\rho_0(E)$ 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

$$\hat{F} = \frac{d}{dt} (e^{i\hat{H}t/\hbar} \Theta(\tilde{\delta}) e^{-i\hat{H}t/\hbar}) \bigg|_{t=0} = \frac{i}{\hbar} [\hat{H}, \Theta(\tilde{\delta})]$$

and the projection function (5) becomes the operator

$$\hat{P}_t = \lim_{t \to +\infty} e^{i\hat{H}t/\hbar} \Theta(\tilde{\delta}) e^{-i\hat{H}t/\hbar}.$$

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,

$$k_{QM}(E) = (2\rho_0(E))^{-1} \int_{-\infty}^{+\infty} dt C_{QM}(E, t)$$

with

$$C_{QM}(E, t) = \text{Tr} \{ \delta(E - \hat{H}) \hat{F} e^{i\hat{H}t/\hbar} \hat{F} e^{-i\hat{H}t/\hbar} \}.$$
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 FFCF 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 $\pm \omega$ and $f - 1$ complex conjugate pairs of imaginary eigenvalues $\pm i\omega_k$, $k = 2, \ldots, f$. 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 $\omega_k$ are not resonant, i.e., $m_2\omega_1 + \cdots + m_f\omega_f \neq 0$ for every nonzero vector of integers $(m_2, \ldots, m_f)$.

A. The classical case

Classical normal form theory provides an algorithm for constructing a (nonlinear) canonical transformation $z \mapsto Z = (Q_1, \ldots, Q_f, P_1, \ldots, P_f)$ 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 $Z$, the $N$th order CNF of the original Hamilton function $H(z)$ assumes the following form

$$H_{CNF}^{(N)}(Z) = K_{CNF}^{(N)}(I, J_2, J_3, \ldots, J_f) = \sum_{|\eta|=n} \sum_{|\eta|=n} \kappa_{n,\eta} J_2^{\eta_1} J_3^{\eta_2} \ldots J_f^{\eta_f},$$

Here $| \eta |$ denotes the floor function, the $\eta = (\eta_1, \ldots, \eta_f)$ are vectors with nonnegative integer components, and norm $|\eta| = \sum_{k=1}^{f} \eta_k$.

$$I = \frac{1}{2} \left( P_1^2 - Q_1^2 \right)$$

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

$$J_k = \frac{1}{2} \left( P_k^2 + Q_k^2 \right), \quad k = 2, \ldots, f,$$

are action integrals of the bath modes which we group together in the vector $J$. The CNF transformation (including the coefficients $\kappa_{n,\eta}$ in Eq. (13)) can be computed in an algorithmic fashion as described in detail in Ref. 19.

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

$$F(Z) = \left. \frac{d}{dt} \delta(Q_1) \right|_{t=0} = - \left. \left[ H_{CNF}^{(N)}(Z) \right] \right|_{t=0} = \delta(Q_1)\nu(I, J) P_1,$$

where

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

Following Eq. (7) the FFCF then takes the form

$$C_{CL}(E, t) = \int d\mathbf{Z} \delta(E - H_{CNF}^{(N)}(\mathbf{Z})) \times \delta(Q_1)\delta(Q_{1t}) \nu(I, J) P_1 P_{1t}, \quad (18)$$

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

$$C_{CL}(E, t) = 2 f(E) \delta(t), \quad (19)$$

where

$$f(E) = \frac{1}{2} \int d\mathbf{Z} \delta(E - H_{CNF}^{(N)}(\mathbf{Z})) \delta(Q_1)\nu(I, J) P_1 |$$

$$= (2\pi)^{-f-1} \int_{\mathbb{R}_+^f} d\mathbf{J} \nu(E - K_{CNF}^{(N)}(I, J)) \nu(I, J)$$

$$= (2\pi)^{-f-1} \int_{I(E, J) > 0} d\mathbf{J}, \quad (20)$$

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

We note that formally the result given by Eq. (19) exists in the literature before (e.g., see Refs. 4 and 26 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 prefactor $f(E)$ 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 Refs. 18–20 a 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 Hamiltonian 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 \( \hat{H}^{(N)}_{\text{QNF}} \) which is of the form
\[
\hat{H}^{(N)}_{\text{QNF}} = \sum_{n=0}^{[N/2]} \sum_{|n|+j=m} \kappa_{n,q,j} \hat{P}_n \hat{Q}_j \hat{P}^n_j / \hbar.
\]
(21)

Here, the notation is the same as in Eq. (13), where in addition the \( j \) are nonnegative integers and
\[
\hat{I} = \frac{1}{2} (\hat{P}_k^2 - \hat{Q}_k^2)
\]
is an operator associated with the reactive mode, and
\[
\hat{J}_k = \frac{1}{2} (\hat{P}_k^2 + \hat{Q}_k^2), \quad k = 2, \ldots, f
\]
are operators associated with the bath modes. In Eqs. (22) and (23) the \( \hat{Q}_k \) and \( \hat{P}_k \), \( k = 1, \ldots, f \), are as usual pairs of conjugate position and momentum operators that satisfy the commutation relations \( [\hat{Q}_k, \hat{P}_k] = i \hbar \delta_{kj} \). 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 Ref. 19.

Since the trace of an operator is invariant under unitary conjugations of the operator we can evaluate Eq. (12) using the QNF to get
\[
C_{\text{QNM}}(E, t) = \text{Tr} \left[ \delta(E - \hat{H}^{(N)}_{\text{QNF}}) F^{(N)}_{\text{QNF}} e^{i \hat{H}^{(N)}_{\text{QNF}} t / \hbar} F^{(N)}_{\text{QNF}} e^{-i \hat{H}^{(N)}_{\text{QNF}} t / \hbar} \right]
\]
(24)
with the flux operator given by
\[
F^{(N)}_{\text{QNF}} = \frac{i}{\hbar} [\hat{P}^{(N)}_{\text{QNF}}, \Theta(\hat{Q}_1)].
\]
(25)

Since the operators \( \hat{I} \) and \( \hat{J}_k \), \( k = 2, \ldots, f \), mutually commute the eigenstates of \( \hat{H}^{(N)}_{\text{QNF}} \) 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,
\[
\hat{H}^{(N)}_{\text{QNF}} | I, n_2, \ldots, n_f \rangle = E | I, n_2, \ldots, n_f \rangle
\]
(26)
with
\[
| I, n_2, \ldots, n_f \rangle = | \psi_I \rangle \otimes | \psi_{n_2} \rangle \otimes \ldots \otimes | \psi_{n_f} \rangle,
\]
(27)
where
\[
\hat{I} | \psi_I \rangle = I | \psi_I \rangle, \quad I \in \mathbb{R},
\]
\[
\hat{J}_k | \psi_{n_k} \rangle = \hbar (n_k + 1/2) | \psi_{n_k} \rangle, \quad n_k \in \mathbb{N}_0,
\]
(28)
and
\[
E = K^{(N)}_{\text{QNF}} (I, \hbar (n_2 + 1/2), \ldots, \hbar (n_f + 1/2)).
\]
(29)

Using the basis given by the eigenstates \( | I, n_2, \ldots, n_f \rangle \) one can now straightforwardly trace out the bath modes in Eq. (24). Indeed, let us define the operator
\[
\hat{H}_{n_2, \ldots, n_f}^{(N)} = \sum_{n=0}^{[N/2]} \sum_{|n|+j=m} \kappa_{n,q,j} \hat{P}_n \hat{Q}_j \hat{P}^n_j / \hbar
\]
\[
\times \left( n_2 + 1 \right)^{n_2} \ldots \left( n_f + 1 \right)^{n_f} \hbar^{n_f - |n| + j},
\]
(30)
parametrized by the \( f - 1 \) nonnegative quantum numbers \( n_2, \ldots, n_f \). Then Eqs. (24) and (25) can be written as
\[
C_{\text{QNM}}(E, t) = \sum_{n_2, \ldots, n_f} \text{Tr} \left[ \delta(E - \hat{H}_{n_2, \ldots, n_f}^{(N)}) \hat{F} e^{i \hat{H}_{n_2, \ldots, n_f}^{(N)} t / \hbar} \hat{F} e^{-i \hat{H}_{n_2, \ldots, n_f}^{(N)} t / \hbar} \right]
\]
(31)
and
\[
\hat{F} = \frac{i}{\hbar} [\hat{P}_{\text{QNF}}, \Theta(\hat{Q}_1)],
\]
(32)
respectively, where, to avoid a cumbersome notation, we have dropped the superscript \( N \) and subscripts \( n_2, \ldots, n_f \) for the operators \( \hat{H} \) and \( \hat{F} \).

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
\[
\hat{H}(a, \lambda) = \hat{h} + a \hat{h}^2, \quad \hat{h} = \frac{1}{2} (\hat{p}^2 - \lambda^2 \hat{q}^2).
\]
(33)
Here \( \lambda \) 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 \( \lambda \) 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 Hamiltonian operator in Eq. (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 \( \hat{H} \))
\[
\hat{h} | \psi_{E, \sigma} \rangle = E | \psi_{E, \sigma} \rangle, \quad E \in \mathbb{R}, \sigma = \pm 1.
\]
(34)
The corresponding wavefunctions are\(^{27, 28}\)
\[
\langle q | \psi_{E, \sigma} \rangle = \frac{1}{2 \pi \hbar} \left( \frac{2 \hbar}{\lambda} \right)^{1/4} \exp \left( \frac{\pi}{4 \lambda \hbar} \right) \Gamma \left( \frac{1}{2} - \frac{E}{\lambda \hbar} \right) \times D_{-(1/2)++i(E/\lambda \hbar)} \left( \sigma e^{-i \frac{\pi}{4}} \sqrt{\frac{2 \lambda}{\hbar} q} \right),
\]
(35)
where $D_\nu$ denotes the parabolic cylinder function of order $\nu$.\cite{20}

The eigenstates are mutually orthogonal,

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

and form a complete basis, i.e.,

$$
\sum_{\sigma=\pm 1} \int_{-\infty}^{+\infty} dE' \, | \psi_\sigma^E \rangle \langle \psi_\sigma'^E | = \mathbf{1},
$$

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

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

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

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 $\lambda$ can in principle be removed by a suitable scaling of the energy). If we denote the two solutions of $E + aE^2 = E$ by

$$
E_\sigma = \frac{1}{2a} \left( -1 + \sigma \sqrt{1 + 4aE} \right), \quad \sigma = \pm 1.
$$

then Eq. (38) becomes

$$
\mathcal{C}_{QM}(E, t, a) = \frac{1}{\sqrt{1 + 4aE}} \int_{-\infty}^{+\infty} dE' \, e^{iE + aE^2 - E \hbar / \hbar} \times \sum_{\sigma,\sigma'} \left| \langle \psi_\sigma'^E | \hat{F} | \psi_\sigma^E \rangle \right|^2.
$$

(40)

if $1 + 4aE > 0$, and $\mathcal{C}_{QM}(E, t, a) = 0$ otherwise. 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

$$
\hat{F} = \frac{i}{\hbar} \left[ \hat{H} + a\hbar^2, \Theta(\hat{q}) \right],
$$

(41)

so that

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

(42)

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

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

(43)

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

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

(44)

We then substitute Eq. (44) into Eq. (40) and use the formula (see Appendix A for its derivation)

$$
\int_{-\infty}^{+\infty} dx e^{i\lambda x^2 + Bx}(1 + Cx)^2 \left| \Gamma(D + iC) \right|^2
= \frac{2\pi \Gamma(2D)}{2^{2D}} \exp \left( \frac{-A \lambda^2}{4} \right)
\times \frac{(\cosh x + iCD \sinh x)^2 + \frac{1}{2} C^2 D}{(\cosh x)^{2D+2}} \bigg|_{x = -i(B/2)}
$$

(45)

with $A = 4a\lambda^2\hbar$, $B = \pi + 2i\lambda\tau$, $C = 2\lambda\alpha / (1 + aE)$, and $D = 1/4$ or $3/4$ to arrive at the central result of our paper:

$$
\mathcal{C}_{QM}(E, t, a) = \frac{(\lambda e^{i\pi/4})}{2\pi^5 \hbar^2 \lambda^2} \Lambda \left( \frac{E}{\lambda\hbar}, \lambda\tau, a\lambda\hbar \right).
$$

(46a)

where

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

(46b)

$$
\epsilon_\sigma(\varepsilon, \alpha) = \frac{1}{2a} \left( -1 + \sigma \sqrt{1 + 4\varepsilon \alpha} \right).
$$

(46c)

$$
\Omega_\sigma(v; \varepsilon, \tau, \alpha)
= \frac{\alpha^2 \exp \left( -i\alpha \tau \frac{\partial^2}{\partial \tau^2} \right)}{(\sinh \tau)^{2v+2}}
\exp \left( -i\alpha \tau \frac{\partial^2}{\partial \tau^2} \right) \left( \epsilon_\sigma \sinh \tau - 2i \nu \cosh \tau \right)^2 - 2\nu.
$$

(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, $\mathcal{C}_{QM}(E, t, a) = 0$ if $1 + 4aE < 0$.) In the following we consider the limits of an harmonic saddle, $a \rightarrow 0$, and short times $\lambda\tau \ll 1$ for which cases $\Omega_\sigma$ 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 $\epsilon_1 = \epsilon + O(\alpha)$ and $\epsilon_{-1} = -1/\alpha - \epsilon + O(\alpha)$. 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

$$\Lambda(\epsilon, \tau, 0) = e^{i(\alpha/2 - \tau)}$$

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

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

$$C_{QM}(\beta, t, a) = \text{Tr} \left[ e^{-\beta \hat{H}} e^{i \hat{H} t / \hbar} e^{-i \hat{H} t / \hbar} \right],$$

(48)

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

$$C_{QM}(\beta, t, 0) = \int_{-\infty}^{+\infty} dE e^{-\beta E} C_{QM}(E, t, 0)$$

$$\equiv \frac{\lambda^2}{4\pi} \frac{\cosh(\lambda t_c) \sinh(\lambda \beta / 2)}{\sinh^2(\lambda t_c) + \cosh^2(\lambda \beta / 2)} \right)^{3/2}$$

(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. 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.

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

$$\Omega_{a}(\nu, \epsilon, \tau, \alpha) \simeq a^2(\epsilon_a^2 D_{2v} - 4i \nu \epsilon_a D_{2v+1} + 2(2v + 1) D_{2v+2})$$

(50)

with

$$D_{\mu}(\tau, \alpha) = \exp \left( -i \alpha \tau \frac{\partial^2}{\partial \nu^2} \right) \frac{1}{\tau^\mu}.$$  

(51)

As shown in Appendix B $D_{\mu}$ in Eq. (51) can be written as

$$D_{\mu}(\tau, \alpha) = e^{\nu^2 / 4} D_{-\mu}(\gamma) \left( \frac{\nu}{\tau} \right)^\mu, \quad \gamma = \left( \frac{\tau}{2a} e^{-i \nu / 2} \right)^{1/2}.$$  

(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 $\Lambda$ in the harmonic case ($a = 0$, 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 $\alpha$ 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 $\alpha$ tends to zero the maximum of 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 $\delta$-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 prefactor (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.

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APPENDIX A: DERIVATION OF EQUATION (45)

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

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

The integral representation given by Eq. (A1) is readily obtained, e.g., from formula 5.13.2 in Ref. 30. Then, denoting the left-hand side of Eq. (45) by $\mathcal{I}$ we get

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

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

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

Now, using

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

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

$$\mathcal{I} = 2\pi \frac{\Gamma(2D)}{2^{2D}} \sum_{n=0}^{\infty} \frac{(-iA)^n}{n!} \frac{\partial^{2n}}{\partial q^{2n}} \frac{1}{\cosh(q/2)} \bigg|_{q = -iB}. \quad (A5)$$

Finally, formally summing the series,

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

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

APPENDIX B: DERIVATION OF EQUATION (52)

Taking into account the identity

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

we rewrite Eq. (51) as

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

Then, using formula 3.462.1 in Ref. 31,

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

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

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It is interesting to note that the QNF approach bears a qualitative relation to the method of locally “good” action-angle variables introduced in Ref. 22 and further developed in Refs. 23–25.

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