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Collective oscillations in the classical nonlinear response of a chaotic system

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We establish a general semiquantitative phase-space picture of the classical nonlinear response in a strongly chaotic system. As opposed to the case of stable dynamics, the response functions decay exponentially at long times. Damped oscillations in response functions are attributed to collective resonances which do not correspond to any periodic classical motions. We calculate analytically the second-order response in a simple chaotic system and demonstrate the relevance of the concept for the interpretation of spectroscopic data.

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Time-domain femtosecond spectroscopy constitutes a powerful tool that probes the electronic and vibrational coherent dynamics of complex molecular systems in the condensed phase [1–4]. Spectroscopic signals are directly related to optical response functions that carry detailed information on the underlying dynamical phenomena. At room temperatures the complexity often originates from slow strongly anharmonic vibrational modes that can be treated within the framework of classical mechanics.

A number of recent studies have been devoted to the nonlinear response in stable (integrable) dynamical systems [5–7]. The classical response functions have been shown to diverge algebraically, while the divergence can be eliminated by invoking a fully quantum description [6,7]. However, at larger energies, away from equilibrium, a generic dynamical behavior can include chaotic features [8]. Moreover, unstable dynamics should be more common due to the stability of chaos with respect to perturbations. It has been argued [9] based on the results of numerical analysis that in chaotic systems classical response functions are converging. In spite of its apparent importance, to the best of our knowledge, the problem of the nonlinear response in strongly chaotic systems has never been addressed by analytical methods. Note that for nonintegrable systems such approaches are rarely feasible, while numerical simulations are complicated by the exponential divergence of stability matrices [9].

In this paper we show that (i) the classical response of a chaotic system exhibits decay and oscillations as a function of the times between the driving pulses and (ii) the Fourier transform of the two-dimensional (2D) second-order response function reveals broad asymmetric peaks as signatures of chaos.

The paper is organized as follows. We first establish a general Liouville-space (i.e., probability distribution space) picture of the nonlinear response in a strongly chaotic system and demonstrate the exponential decay of response functions at long times. Motivated by Sinai's idea originally applied to a billiard [10], we further argue that classical dynamics on an energy shell with g forbidden regions can be qualitatively represented by free motion on a curved Riemann surface of genus g. To illustrate the general picture, we analytically calculate the second-order response for motion on a surface of constant negative curvature. Finally, we demonstrate that 2D spectroscopic data on strongly chaotic systems can be interpreted in terms of collective Ruelle-Pollicott (RP) resonances that characterize the spectrum of the coarse-grained Liouville operator [11,12].

A system driven by a time-dependent external field $\mathcal{E}(t)$ is described by the Hamiltonian $H_T = H - f\mathcal{E}(t)$ with the phase-space function $f(\boldsymbol{\eta})$, which represents the dipole (see, e.g., Ref. [9]). The response functions $S^{(n)}$ that depend on n time intervals describe the expansion of the measured signal $\langle f(\boldsymbol{\eta}(t))\rangle = \int d\boldsymbol{\eta}\rho f$ in a functional series in $\mathcal{E}$. The second-order response function reads

$$S^{(2)}(t_1,t_2) = \partial_{t_1} \int d\boldsymbol{\eta} f e^{-\hat{L}t_2}\{f, e^{-\hat{L}t_1} f \partial_E \rho_0\}, \quad (1)$$

where ρ_0 and $\hat{L} = \{H, \cdot\}$ are the equilibrium distribution and the unperturbed Liouville operator, respectively. The braces denote the Poisson bracket.

We propose the following schematic picture for the classical response in the Liouville space of a strongly chaotic system (see Fig. 1). We interpret the second-order response in Eq. (1) as a convolution of the distributions

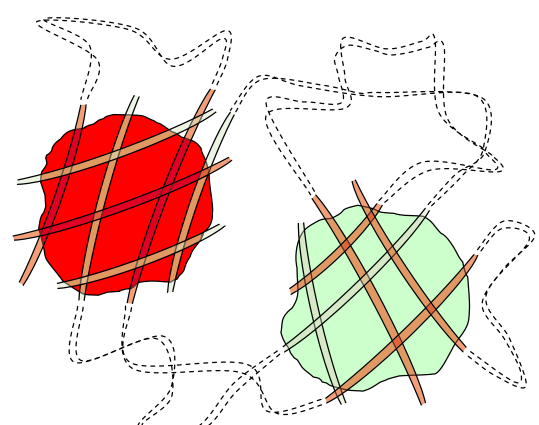

FIG. 1. (Color online) Schematic cross section of the phase space along the surface given by the stable and unstable directions. The initial distribution of f is presented by two regions where its values have opposite signs (red or dark gray and green or light gray). As time elapses the distribution elongates along the unstable direction and contracts along the stable one.

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$f_-(\boldsymbol{\eta})=\exp(\hat{L}t_2)f$ (propagated backward) and $\xi^j\partial_j f_+(\boldsymbol{\eta})$, where $f_+=\exp(-\hat{L}t_1)f\partial_E\rho_0$ and $\xi^j\partial_j=\{f,\cdot\}$. Since $\int d\boldsymbol{x}f=0$, we can assume for simplicity that f is nonzero in two separate phase-space regions, where it adopts positive and negative values of similar magnitudes. Strongly chaotic dynamics during long time makes the shapes of the regions similar to ribbonlike fettuccine: elongated along the unstable direction by a factor $\sim e^{\lambda t}$, narrowed along the stable one $\sim e^{-\lambda t}$ (λ is the Lyapunov exponent), and unchanged along the flow [13]. The fettuccine of f_+ and f_- are aligned along the unstable and stable directions of the forward dynamics, respectively. Therefore, their overlap is represented by a large set of $N\sim e^{\lambda(t_1+t_2)}$ small disconnected regions, each of volume $v\sim e^{-\lambda(t_1+t_2)}$. Since chaotic mixing results in irregular alternation of oppositely "charged" ribbons, the contribution of a single region can have either sign with magnitude $\propto v$. The typical absolute value of their sum is $\sqrt{N}v\sim e^{-\lambda(t_1+t_2)/2}$. Yet this is not the end of the story since the derivative $\xi^j\partial_j$ of a sharp feature along the stable direction can create exponentially large $\sim e^{\lambda t_1}$ factors. This is the Liouville-space signature of the exponentially growing components of the stability matrix, which affects the response starting with second order [9,14]. However, the divergent terms cancel out: decomposing $\boldsymbol{\xi}=\boldsymbol{\xi}_0+\boldsymbol{\xi}_++\boldsymbol{\xi}_-$ along the flow, and unstable and stable directions, we note that only the last term is potentially dangerous. Calculating the corresponding component of the overlap integral by parts we arrive at two contributions: one contains the derivative along the fettuccine $\xi_-^j\partial_j f_-$ and is hence negligible, whereas div $\boldsymbol{\xi}_-$ in the other provides a time-independent factor. This results in a physical long-time asymptotic behavior $|S^{(2)}|\sim e^{-\lambda(t_1+t_2)/2}$ of the second-order response. The same approach allows us to estimate the response functions of higher orders and find their exponential decay. We note that it is the mixing property of the chaotic dynamics that outweighs the effect of the exponential growth in certain components of the stability matrix and ensures the convergence of the response.

To illustrate the general picture of response in a chaotic system we calculate the linear and second-order classical response functions for free motion on a Riemann surface M^2 of constant negative (Gaussian) curvature [8,15,16]. The classical free-particle Hamiltonian is given by

$$H=(1/2m)g^{ik}p_ip_k=\zeta^2/2m, \tag{2}$$

where ζ and g_{ik} are the absolute value of momentum and the metric tensor. The Hamiltonian dynamics preserves a subspace with fixed energy described by a smooth compact 3D manifold M^3 whose points $\boldsymbol{x}$ include two coordinates and the momentum direction angle θ. Hereafter, we use dimensionless units so that $m=1$, the curvature $K=-1$, and $\zeta=1$ (when the energy is fixed).

Although apparently abstract, the model is related to more tangible dynamics. The trajectories of a multiparticle system with energy E in an arbitrary potential $U(\boldsymbol{r})$ are known to be the same as for free motion in a curved space with the metric $g_{ik}=[1-U(\boldsymbol{r})/E]\delta_{ik}$ [8,15]. If the metric curvature is negative, one can expect chaotic behavior due to the exponential divergence of trajectories. In addition, when the motion is finite (bounded), the accessible part of the configuration space at a given energy can be multiply connected. In the simplest case of two coordinates the motion occurs inside a disklike region punctured by g forbidden islands. A fraction of trajectories approaches the boundaries so close that this can be qualified as reflection. Utilizing Sinai's argument [10], reflection can be interpreted as the transition to an antipode replica of the accessible region glued to its original counterpart via the boundaries [18]. This results in a compact surface of genus g—i.e., with the topology of a sphere with g handles. For $g>1$ the average Gaussian curvature is negative, which causes an unstable (hyperbolic) dynamics.

Free motion on a compact surface of constant negative curvature can be treated analytically due to strong dynamical symmetry (DS), which originates from the SO(2,1) group action in phase space M^3 [12,16–18]. Its infinitesimal counterpart so(2,1) is determined by three generators: infinitesimal rotation $\sigma_z=\partial/\partial\theta$ in momentum space, the vector field σ_1 that describes the geodesic flow, and their commutator $\sigma_2=[\sigma_1,\sigma_z]$. DS with respect to the action of the group $G\cong SO(2,1)$ does not mean symmetry in a usual sense, but rather reflects the fact that the system dynamics is given by an element σ_1 of the corresponding so(2,1) algebra.

DS implies that the space of phase-space distributions constitutes a representation of SO(2,1) and, being decomposed into a sum of irreducible representations, provides a set of uncoupled evolutions. Unitary irreducible representation of SO(2,1) are well known and can be conveniently implemented in terms of functions $\Psi(u)$ on a circle [19]. Principal series representations relevant for our calculations are labeled by imaginary parameter s with the Liouville operator $\sigma_1=\sin u\partial_u+(1/2-s)\cos u$. The aforementioned decomposition identifies the angular harmonic $\Psi_k(u)=e^{iku}$ on a circle with a phase-space distribution $\psi_k(\boldsymbol{x};s)$ with angular momentum k, $\sigma_z\psi_k(\boldsymbol{x};s)=ik\psi_k(\boldsymbol{x};s)$, whereas any relevant distribution can be decomposed in the angular harmonics $\psi_k(\boldsymbol{x};s)$. The discrete spectrum $\{s\}$ is related to the spectrum $\{\lambda\}$ of the Laplacian operator in M^2 as $\lambda=1/4-s^2$, whereas $\psi_0(\boldsymbol{x};s)$ are the corresponding eigenfunctions [12,16]. The dipole f, being a function in M^2, can be viewed as a phase-space function independent of both ζ and θ and hence expanded as a sum over the principal series representations $f=\Sigma_sB_s\psi_0(\boldsymbol{x};s)$.

The integrand in the response function (1) involves undriven evolution described by $e^{-\hat{L}t}$ and interaction with the driving field represented by the Poisson bracket with f. The evolution part is straightforward, once the DS is established; the problem has been treated, e.g., in Ref. [12] in the context of two-point correlation functions. The second task requires additional effort, since interaction with the field mixes different representations. Handling the second task is the main technical result of this paper.

Due to DS, the distributions $e^{-\hat{L}t}\psi_0(\boldsymbol{x};s)$ can be decomposed in the basis vectors $\psi_k(\boldsymbol{x};s)$ with the *same value* of s [12,16,18,20],

$$e^{-\hat{L}t}\psi_0(\boldsymbol{x};s) = \sum_{k=-\infty}^{+\infty} A_k(t;s)\psi_k(\boldsymbol{x};s), \tag{3}$$

and the coefficients $A_k(t;s)$ can be calculated explicitly using the effective dynamics in the circle, which yields

$$A_k(t;s) = \frac{2(-1)^k(1-e^{-2t})^k\Gamma(k+1/2-s)}{\sqrt{\pi}\Gamma(1/2-s)}e^{-t/2} \times \mathrm{Re}\left[\frac{\Gamma(s)e^{st}}{\Gamma\left(k+\frac{1}{2}+s\right)}{}_2F_1\left(k+\frac{1}{2}-s,k+\frac{1}{2},1-s,e^{-2t}\right)\right],$$

where ${}_2F_1$ is the Gauss hypergeometric function.

The linear response function can be conveniently expressed as $S^{(1)}(t)\propto\partial_t A_0(t;s)$ [14]. For large t the linear response function shows damped oscillations $e^{(\pm s-1/2)t}$. The expansion in powers of e^{-2t} constitutes a converging series and corresponds to RP resonances [12].

To the best of our knowledge, the second-order response function in strongly chaotic systems has never been calculated before. The calculation can be substantially simplified by propagating the observable f in Eq. (1) backwards in time and making use of $(e^{-\hat{L}t_2})^\dagger = e^{\hat{L}t_2}$. Then we apply Eq. (3) to decompose $e^{\hat{L}t_2}\psi_0(\boldsymbol{x};s)$ in $\psi_k(\boldsymbol{x};s)$ and $e^{-\hat{L}t_1}\psi_0(\boldsymbol{x};s)$ in $\psi_l(\boldsymbol{x};s)$. The integration over the reduced phase space includes an integral over the momentum direction θ, which results in a vanishing of all terms with $k\neq l\pm 1$. The second-order response function consists of several contributions $S^{(2)}=\Sigma_j\Sigma_{p,q,r}B_pB_qB_r\Sigma_{k=0}^{\infty}(-1)^k S_{j,k}^{(2)}$ of similar form [18]: e.g.,

$$S_{1,k}^{(2)} = (-1)^k k\left(k+\frac{1}{2}-p\right)a_k^{pqr}A_{k+1}^*(t_2;p)\frac{\partial A_k(t_1;r)}{\partial t_1},$$

with the matrix elements

$$a_k^{s_1s_2s_3} = \int_{M^3} d\boldsymbol{x}\,\psi_k^*(\boldsymbol{x};s_1)\psi_0(\boldsymbol{x};s_2)\psi_k(\boldsymbol{x};s_3). \tag{4}$$

Computing the matrix elements and summation over k are two main problems in the calculation. The first one is addressed by establishing recurrence relations for the coefficients (4) that allow expressing all of them via a few "initial conditions": e.g., $a_0^{s_1s_2s_3}$. This is achieved by combining the integration-by-part rule

$$\int_{M^3} d\boldsymbol{x} f(\boldsymbol{x})\sigma_l g(\boldsymbol{x}) = -\int_{M^3} d\boldsymbol{x}[\sigma_l f(\boldsymbol{x})]g(\boldsymbol{x}) \tag{5}$$

[which follows from DS and is valid for any phase-space functions $f(\boldsymbol{x})$ and $g(\boldsymbol{x})$ and any generator σ_l] with the ladder properties $\sigma_\pm\psi_k(\boldsymbol{x};s)=(\pm k+1/2-s)\psi_{k\pm1}(\boldsymbol{x};s)$ of the two anti-Hermitian-conjugated ladder operators $\sigma_\pm=\sigma_1\pm i\sigma_2$ and $\sigma_\pm^\dagger=\sigma_\mp$. For instance, in the simplest case $s_1=s_2=s_3=s$, the recurrence relations read

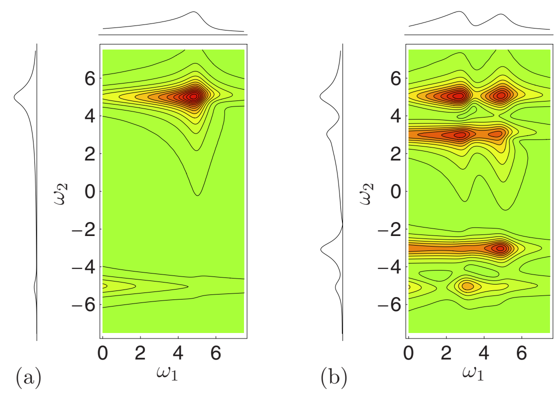

FIG. 2. (Color online) Absolute value of the 2D Fourier transform of the second-order response function: (a) single resonance $s=5i$ and (b) linear combination of terms with two resonances $s_1=3i$ and $s_2=5i$. The response is evaluated for the equilibrium phase-space density with $\partial\rho_0/\partial E\propto\delta(E-1/2)$. Linear plots show cross sections at $\omega_1=\omega_2=5$.

$$a_{k+1} = \frac{8k^2+1-s^2}{(2k+1)^2-s^2}a_k - \frac{(2k-1)^2-s^2}{(2k+1)^2-s^2}a_{k-1}, \tag{6}$$

and all coefficients a_k are expressed via a_0 due to the symmetry $a_k=a_{-k}$. In this case we find the asymptotic behavior $a_k\propto k^{-1/2\pm s}$ for $k\to\infty$. The set of coefficients a_0, as well as the spectrum $\{s_\alpha\}$, are attributes of a particular Riemann surface. Riemann surfaces of constant negative curvature have genus $g>1$ and are classified by the so-called moduli spaces whose dimensions grow linearly in g. Therefore, any finite set of spectral elements s_α and matrix elements $a_0^{s_\alpha s_\beta s_\gamma}$ can be implemented for some particular Riemann surface, and we treat them as independent parameters.

The second problem is addressed using the following approach. The convergence of the series over k is ensured by the dependence $A_k(t;s)\propto\exp(-2ke^{-t})$ for large k. The series is almost sign alternating, and the dependence of the summand magnitude on k becomes smoother with increasing k, independently of t. This allows for an efficient regrouping procedure to evaluate the series without summation of the exponentially increasing with t number of terms. The procedure also works in any order of e^{-t_1} and e^{-t_2} obtained from the hypergeometric expansions of $A_k(t;s)$ [20]. Our study of the response can be extended by adding Langevin noise to classical Hamiltonian dynamics, which is equivalent to adding a certain second-order (diffusion) differential operator to the Liouville operator: $\hat{\mathcal{L}}=-\kappa\hat{D}+\hat{L}$, where κ is given by the noise intensity. In the limit $\kappa\to 0$ the RP resonances are identified as the eigenvalues of the Fokker-Planck operator $\hat{\mathcal{L}}$, whereas the corresponding spectral decompositions of $S^{(1)}(t)$ and $S^{(2)}(t_1,t_2)$ reproduce the expressions for the classical response obtained above [21].

The absolute value of the 2D Fourier transform of the second-order response function presented in Fig. 2 shows diagonal and cross peaks, as well as a stretched along the ω_1 direction feature [18]. The latter originates from damped time-domain oscillations with variable period and can be interpreted as a signature of chaos in the underlying dynamics. Also note that in chaotic systems the peak frequencies may not be attributed to any particular periodic motions, although they can be expressed in terms of all periodic orbits via the dynamical ζ function [11]. Therefore, they can be referred to as *collective chaotic resonances*.

Chaotic features are quite generic for molecular systems. We believe that systems of hydrogen bonds [22] are promising examples to observe complex potentials that may induce chaotic behavior. We demonstrated that spectroscopic signals from a chaotic system have peaks corresponding to RP resonances that can be naively assigned to periodic motions coupled to the environment. We propose the asymmetry of the peaks in the 2D spectrum as a signature of chaos, since usually this peak shape cannot be explained by the interaction with the multimode harmonic bath (multimode Brownian oscillator). Note that RP resonances can show up and hence be spectroscopically observed in the relaxation dynamics of more general systems with mixed phase space [23].

In this paper we developed a general semiquantitative picture of the classical nonlinear response in a chaotic system and demonstrated the exponential long-time convergence of the response functions. The latter has been attributed to the exponential behavior of the stability matrix whose growing components combined with the mixing property assist the convergence. The picture is corroborated by the calculation of the second-order response for free motion on a surface of constant negative curvature. We believe that this is the first analytical calculation of classical nonlinear response for a strongly chaotic system. We showed that the diagonal and off-diagonal peaks with pronounced stretched features in the 2D spectrum can be interpreted in terms of collective (Ruelle-Pollicott) resonances.

In the future we plan to extend our work to numerical studies of multidimensional motion in a potential with a number of forbidden regions, starting with the simplest 2D case. In addition, the technique developed in the paper can be applied to describe the dynamics of a quantum electronic or high-frequency IR transition coupled to a low-dimensional classical chaotic system as opposed to a multimode harmonic bath.

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