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Classical chaos and fluctuation-dissipation relations for nonlinear response

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The classical nonlinear optical response is expressed in a form that closely resembles the fluctuation-dissipation theorem. The nth-order response is shown to depend on interferences among n closely lying trajectories. The relevant dynamical information on the vicinity of a given trajectory can be recast using the stability matrix related to the Lyapunov exponents. No such interference exists in the linear response, and the nonlinear response is consequently a much more sensitive probe for classical chaos. Sequences of multiple femtosecond pulses can be designed to directly probe the stability matrix.

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Nonlinear optical measurements are usually interpreted by expanding the polarization P in powers of the incoming electric field E. To nth order we have

$$P^{(n)}(t)=\int_{-\infty}^{t}d\tau_n\int_{-\infty}^{\tau_n}d\tau_{n-1}\cdots\int_{-\infty}^{\tau_2}d\tau_1 E(\tau_n)\cdots E(\tau_1)\times S^{(n)}(t,\tau_n,\ldots,\tau_1). \quad (1)$$

Quantum mechanically, the nonlinear response function $S^{(n)}(t,\tau_n,\ldots,\tau_1)$ is given by a combination of $(n+1)$-order correlation functions of the dipole operator V,

$$S^{(n)}=\left(\frac{i}{\hbar}\right)^n \mathrm{Tr}\{V(t)[V(\tau_n),\ldots,[V(\tau_2),[V(\tau_1),\rho]]\cdots]\}. \quad (2)$$

Equation (2) contains 2^n terms representing all possible "left" and "right" actions of the various commutators. Each term corresponds to a Liouville-space path and can be represented by a double-sided Feynman diagram [1]. The various correlation functions interfere and this gives rise to many interesting effects such as new resonances. The $(i/\hbar)^n$ factor indicates that individual correlation functions do not have an obvious classical limit. The entire response function must, however, have a classical limit. When the various correlation functions are combined, the $(i/\hbar)^n$ factor is canceled as $\hbar\to 0$, and one obtains the classical response, independent of $\hbar$. The elimination of $\hbar$ for higher nonlinearities requires a more delicate interference among all 2^n correlation functions.

The linear $(n=1)$ response is expressed via the two-time correlation function of the dipole operator

$$S^{(1)}(t,\tau_1)=\frac{i}{\hbar}[\langle V(t)V(\tau_1)\rangle-\langle V(\tau_1)V(t)\rangle]. \quad (3)$$

The development of classical and semiclassical methods for computing directly the necessary combinations of correlation functions rather than the individual ones is an interesting open problem. For the linear response this is accomplished by the fluctuation-dissipation theorem [2]

$$S^{(1)}(t,\tau_1)=-\beta\frac{d}{d\tau_1}\langle V(t)V(\tau_1)\rangle, \quad (4)$$

where $\beta=(kT)^{-1}$.

Unlike the quantum response (3), which contains an interference of two Liouville-space paths, the classical expression (4) contains no interference and may be directly computed using classical trajectories which sample the initial density matrix [3]. Recent developments in femtosecond spectros-

copy [4,5] require the classical evaluation of nonlinear response functions. For example, multiple infrared pulse measurements in liquids probe intermolecular and intramolecular nuclear motions, which are essentially classical. Generalized optical Kerr techniques conducted using off-resonant optical pulses [7–11] reveal the multidimensional nuclear spectral densities. The coupling with the field $-VE$ is replaced in this case by an effective coupling $-\alpha E^2$, and the response can be calculated using Eq. (2) by replacing the dipole operator V with the electronic polarizability α, and substituting $E^2(\tau)$ for each $E(\tau)$. These techniques are the analogs of multidimensional NMR spectroscopy where nonlinear response functions are commonly used to selectively probe features and dynamical information that is not accessible by linear techniques [12]. Coherent control of atomic and molecular events [13] is another application where classical intuition for nonlinear spectroscopy should be very useful. The classical simulation of these measurements requires the generalization of the fluctuation-dissipation theorem to nonlinear response. This is the primary objective of this paper. We will show that the classical nonlinear response contains an intrinsic interference among closely lying trajectories originating from the same region in phase space. This provides a direct probe for the stability matrix and the Lyapunov exponents [14]. In contrast, the fluctuation-dissipation theorem for the linear response implies that each phase-space point contributes only a single trajectory, and no interference exists beyond averaging over the initial phase-space distribution. The present arguments are not limited to optical response, and apply to an arbitrary external field.

The response function $S^{(n)}(t,\tau_n,\ldots,\tau_1)$ is written in the Heisenberg picture as

$$S^{(n)}(t,\tau_n,\ldots,\tau_1)=\langle V(t)\mathscr{V}(\tau_n)\cdots\mathscr{V}(\tau_1)\rangle. \tag{5}$$

Here the averaging is carried out with respect to the initial density function $\rho^{(0)}(\mathbf{x})$, where $\mathbf{x}=(\mathbf{p},\mathbf{q})$ denotes the phase-space coordinates, $V(t)$ is the dipole moment, and $\mathscr{V}(\tau_k)$ the Liouville-space dipole operators that act on an arbitrary function of $\mathbf{x}$ through the Poisson bracket. We use the general form of the Poisson bracket:

$$\mathscr{V}f(x)\equiv\{V(x),f(x)\}=\sum_{jk}\omega_{jk}\frac{\partial V(x)}{\partial x_j}\frac{\partial f(x)}{\partial x_k}, \tag{6}$$

where ω_{jk} may assume the values 0, 1, and -1. The fluctuation-dissipation theorem is obtained by noting that the initial canonical density matrix, $\rho^{(0)}(\mathbf{x})=Z^{-1}\exp\{-\beta H\}$, depends on $\mathbf{x}$ only through the Hamiltonian, and

$$\mathscr{V}\rho^{(0)}=-\beta\{V,H\}\rho^{(0)}=-\beta\frac{dV}{dt}\rho^{(0)}.$$

We now turn to the second-order response

$$S^{(2)}(t,\tau_2,\tau_1)=\langle V(t)\mathscr{V}(\tau_2)\mathscr{V}(\tau_1)\rangle. \tag{7}$$

Noting that

$$\begin{aligned}\mathscr{V}(\tau_2)\mathscr{V}(\tau_1)\rho^{(0)}(x)&=-\beta\frac{d}{d\tau_1}\{V(\tau_2),V(\tau_1)\rho^{(0)}(x)\}\\&=\beta^2\frac{d^2}{d\tau_2 d\tau_1}V(\tau_2)V(\tau_1)\rho^{(0)}(x)\\&\quad-\beta\frac{d}{d\tau_1}\{V(\tau_2),V(\tau_1)\}\rho^{(0)}(x),\end{aligned}$$

yields

$$\begin{aligned}S^{(2)}(t,\tau_2,\tau_1)&=\beta^2\frac{d^2}{d\tau_2 d\tau_1}\langle V(t)V(\tau_2)V(\tau_1)\rangle\\&\quad-\beta\frac{d}{d\tau_1}\langle V(t)\{V(\tau_2),V(\tau_1)\}\rangle.\end{aligned} \tag{8}$$

To evaluate the Poisson bracket that appears in (8), we need to calculate derivatives of $V(\tau_1)$ with respect to x_j at time τ_2, that is, we need to relate the x derivatives at different times. The derivatives propagate by the formula

$$\frac{\partial}{\partial x_j(\tau_2)}=M_{jk}(\tau_2,\tau_1)\frac{\partial}{\partial x_k(\tau_1)},$$

$$M_{jk}(\tau_2,\tau_1)\equiv\left\{\frac{\partial x_k(\tau_1)}{\partial x_j(\tau_2)}\right\},$$

where the summation over the repeated indices is implied. The matrix M, which relates small deviations δx_j to δx_k at different times, is known as the stability matrix [14]. We can finally rewrite (8) as

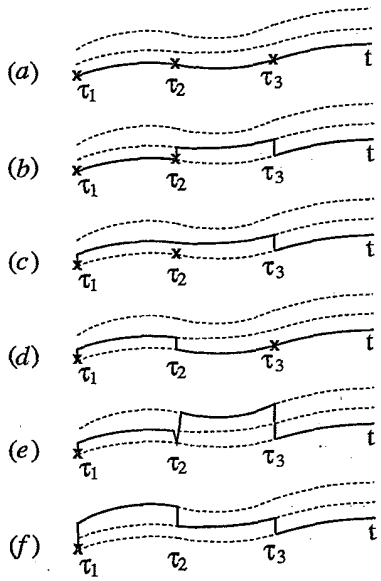

FIG. 1. Interference of nearby trajectories in $S^{(3)}$. Paths (a)–(f) correspond to the six terms in (11), respectively. Crosses at times τ_j, $j=1,2,3$, stand for derivatives with respect to τ_j.

$$S^{(2)}(t,\tau_2,\tau_1)=\beta^2\frac{d^2}{d\tau_2 d\tau_1}\langle V(t)V(\tau_2)V(\tau_1)\rangle - \beta\frac{d}{d\tau_1}\langle \omega_{ij}M_{jk}(\tau_2,\tau_1)V(t)V_i'(\tau_2)V_k'(\tau_1)\rangle, \tag{9}$$

where $V_j'\equiv\partial V/\partial x_j$. The first term, related to the three-point dipole correlation function, is a direct generalization of the fluctuation-dissipation theorem. It can be evaluated by following a single trajectory for each initial phase-space point. The second term is much more interesting, and can be interpreted as follows: for each initial phase-space point we need to launch two trajectories with very close initial conditions. (For $S^{(n)}$ we need n trajectories; see Fig. 1.) The nonlinear response is obtained by adding the contributions of these trajectories and letting them interfere.

The third-order response is similarly given by

$$\begin{aligned}S^{(3)}(t,\tau_3,\tau_2,\tau_1)=&-\beta^3\frac{d^3}{d\tau_3 d\tau_2 d\tau_1}\langle V(t)V(\tau_3)V(\tau_2)V(\tau_1)\rangle\\&+\beta^2\frac{d^2}{d\tau_2 d\tau_1}\langle V(t)\{V(\tau_3),V(\tau_2)V(\tau_1)\}\rangle\\&+\beta^2\frac{d^2}{d\tau_3 d\tau_1}\langle V(t)V(\tau_3)\{V(\tau_2),V(\tau_1)\}\rangle\\&-\beta\frac{d}{d\tau_1}\langle V(t)\{V(\tau_3),\{V(\tau_2),V(\tau_1)\}\}\rangle.\end{aligned} \tag{10}$$

Using the stability matrix we finally have

$$\begin{aligned}S^{(3)}(t,\tau_3,\tau_2,\tau_1)=&-\beta^3\frac{d^3}{d\tau_3 d\tau_2 d\tau_1}\langle V(t)V(\tau_3)V(\tau_2)V(\tau_1)\rangle+\beta^2\frac{d^2}{d\tau_2 d\tau_1}\langle \omega_{ij}M_{jk}(\tau_2,\tau_3)V(t)V_i'(\tau_3)V_k'(\tau_2)V(\tau_1)\rangle\\&+\beta^2\frac{d^2}{d\tau_2 d\tau_1}\langle \omega_{ij}M_{jk}(\tau_1,\tau_3)V(t)V_i'(\tau_3)V(\tau_2)V_k'(\tau_1)\rangle\\&+\beta^2\frac{d^2}{d\tau_3 d\tau_1}\langle \omega_{ij}M_{jk}(\tau_1,\tau_2)V(t)V(\tau_3)V_i'(\tau_2)V_k'(\tau_1)\rangle\\&-\beta\frac{d}{d\tau_1}\langle \omega_{nl}\omega_{ij}M_{lm}(\tau_2,\tau_3)M_{jk}(\tau_1,\tau_2)V(t)V_n'(\tau_3)V_{im}''(\tau_2)V_k'(\tau_1)\rangle\\&-\beta\frac{d}{d\tau_1}\langle \omega_{nl}\omega_{ij}M_{lm}(\tau_1,\tau_3)M_{jk}(\tau_1,\tau_2)V(t)V_n'(\tau_3)V_i'(\tau_2)V_{km}''(\tau_1)\rangle.\end{aligned} \tag{11}$$

Here $V_{im}''\equiv\partial^2 V/\partial x_i\partial x_m$. The quantum response function contains a 2^n-fold interference of the various correlation functions. The classical interference is of a very different nature: first, $S^{(n)}$ contains $n!$ terms. In addition, each term may depend on a bundle of up to n nearby trajectories (depending on the number of stability matrices M). This additional interference, coming from nearby trajectories, is illustrated in Fig. 1 for the third-order response [paths (a) through (f) correspond respectively to the six terms in (11)]. Path (a) contains no additional interference; this is the fluctuation-dissipation contribution. Paths (b)–(d) contain an interference from one pair of trajectories each, which is expressed by the stability matrix. The terms (e) and (f) involve three trajectories; the interference comes from two pairs of trajectories for each time interval, which leads to a product of two stability matrices in each term. The same arguments apply immediately to higher-order response functions. In general, the nth-order response is expressed via the set of the stability matrices $M(\tau_i,\tau_j)$ for each pair of the subscripts $i,j=1,\ldots,n$.

The stability matrix carries the necessary information related to the vicinity of the trajectory and provides a very efficient numerical procedure for computing the response function. Note that the response function depends on $M(\tau_i,\tau_j)$ for all values of τ_i and τ_j. By running a single trajectory we can first calculate the M matrix as a function of time with reference to the initial time τ_1. For a single degree of freedom $x=(q,p)$ it may be obtained from

$$\dot{M}=\begin{pmatrix}-\dfrac{\partial^2 H}{\partial q^2} & -\dfrac{\partial^2 H}{\partial q\,\partial p}\\ \dfrac{\partial^2 H}{\partial p\,\partial q} & \dfrac{\partial^2 H}{\partial p^2}\end{pmatrix}M. \tag{12}$$

The generalization to arbitrary number of degrees of freedom in terms of the Hessian matrix is straightforward. We can then use the relation $M(\tau_i,\tau_j)=M^{-1}(\tau_j,\tau_1)M(\tau_i,\tau_1)$ to obtain the matrix for arbitrary pairs of times along the trajectory.

Unlike the classical linear response which contains no interference (just simple averaging over the initial density matrix), the nonlinear response shows an interesting classical interference. The stability matrix plays an important role in the field of classical chaos [14]. The sign of its eigenvalues (related to the Lyapunov exponents) controls the chaotic na-

ture of the system. Numerous studies have been performed in order to identify the signatures of chaos in linear spectra. Level statistics has been one of the key quantities investigated. Equation (9) shows that the nonlinear response is a much more natural measure of chaos since it provides a direct probe for the stability matrix. The possible divergence of the linear response at long times has been pointed out by van Kampen as a fundamental limitation of response theory. The argument made is that the effect of a weak external field on a nonlinear dynamical system at long times may not be treated perturbatively [15]. Despite this formally correct argument, linear response functions are usually well behaved. The reason is that while individual trajectories with a fixed initial condition may be sensitive, the corresponding divergence of the response at long times is canceled once averaging over the initial density matrix is carried out. Therefore, phase-space averaging eliminates the difficulties pointed out by van Kampen, and guarantees that the response will remain finite at all times. This point was illustrated in a recent numerical study of the nonlinear response of a quartic oscillator with the potential kr^4 [16]. Prior to thermal averaging, the third-order nonlinear response function for this system is unbounded and grows linearly in time. Upon averaging, this behavior changes dramatically and the response function properly decays at long times.

We shall now consider possible models where these effects could be observed. For the linearly driven harmonic oscillator all nonlinear response functions vanish identically due to interference among Liouville-space paths. The simplest model that shows a finite nonlinear response is a nonlinearly driven harmonic oscillator where the dipole moment is a nonlinear function of the coordinate. This model can be studied analytically both quantum mechanically and classically [5,6]. In this case the response oscillates with time and remains finite even before any thermal averaging. This is a peculiar feature of the harmonic oscillator, for which the evolution and stability matrices are given by the same functions. Thus the two terms as in (9) are not fundamentally different in this case. The linear divergence of the response at long times found in [16] should be typical for integrable systems. For a nonintegrable (chaotic) system, the growth of the nonlinear response functions should be exponential [14].

By a proper choice of a multiple femtosecond pulse sequence [4,13,17,19] it should become possible to design nonlinear measurements that select a particular time interval and probe a specific element of the stability matrix. For anharmonic systems the elements of the stability matrix depend on the starting point of the trajectory in phase space and can provide a direct measure for chaotic behavior. Furthermore, optical measurements using carefully shaped pulses with controlled phases have the capacity to prepare nuclear wave packets confined to a specified region in phase space, thus eliminating the thermal averaging [17,18]. Dramatic signatures in the nonlinear response may then be anticipated in systems such as I_2 or Na_2 [19]. Nonlinear spectroscopy could thus provide a direct test for the coherent control of nuclear dynamics [13,19]. Finally, we note that signatures of nonlinear response can also be found in electronically resonant techniques such as electronic photon echoes and dichroism measurements [1,17]. The arguments made in this paper apply to such measurements as well. However, the analysis of these systems is complicated by the interplay of electronic and nuclear coherence. For simplicity and clarity we restricted our analysis to electronically off-resonant measurements.

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