Classical Divergence of Nonlinear Response Functions

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The time divergence of classical nonlinear response functions reveals the fundamental difficulty of dynamic perturbation based on classical mechanics. The nature of the divergence is established for systems in regular motions using asymptotic decomposition of Fourier integrals. The asymptotic analysis shows that the divergence cannot be removed by phase-space averaging such as the Boltzmann distribution function. The implications of this study are discussed in the context of the conceptual development of quantum-classical correspondence in dynamic response.

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Introduction.—Response theory predicts the response of a physical system to an external disturbance perturbatively and forms the theoretical basis of describing many experimental measurements. It was first pointed out by van Kampen that even a weak perturbation leads to the failure of classical nonequilibrium perturbation theory at sufficiently long times [1]. Despite this argument, the application of linear response theory does not lead to practical difficulties because phase-space averaging over the initial density matrix with Boltzmann distribution cancels the divergence at long times. Yet, thermal distribution may not remove the divergence of nonlinear response functions. The purpose of this Letter is to study the divergence of classical response functions of quasiperiodic systems. The analytical treatment of the behavior of the classical response function has not been studied except for a few exactly solvable anharmonic systems such as quartic [2] and Morse [3,4] oscillators, showing that in some cases classical response functions diverge at long times. However, the divergent behavior in the general case of systems with regular dynamics has not been systematically investigated. The proof of the divergence has important implications for the conceptual development of quantum-classical correspondence in response theory and can be established by employing the methods of Fourier expansion and asymptotic decomposition.

The response function is well defined quantum mechanically in eigenstate space and is expressed by a set of nested commutators

$$R_q^{(n)}(t_n, \ldots, t_1) = \left(\frac{\iota}{\hbar}\right)^n \langle [[\ldots[\hat{\alpha}(\tau_n), \hat{\alpha}(\tau_{n-1})], \ldots, \hat{\alpha}(\tau_1)], \hat{\alpha}(0)]\rangle, \tag{1}$$

where $\tau_n = \sum_{i=1}^n t_i$ and $\hat{\alpha}(\hat{\mathbf{x}}(t), \hat{\mathbf{p}}(t))$ is the system polarizability or dipole momentum operator. The classical limit of the quantum response function (1) is usually obtained in the limit of $\hbar \to 0$ by replacing quantum commutators with Poisson brackets and neglecting higher order terms in the Plank constant,

$$R_c^{(n)}(t_n, \ldots, t_1) = (-1)^n \langle \{\{\ldots\{\alpha(\tau_n), \alpha(\tau_{n-1})\}, \ldots, \alpha(\tau_1)\}, \alpha(0)\}\rangle, \tag{2}$$

where $\{\ldots\}$ are Poisson brackets. Yet, thus defined, classical response theory has several difficulties. The expression (2) contains stability matrices which grow in time linearly for integrable systems [2] and exponentially for chaotic systems [5]. The growth results in the divergent behavior of classical response functions for a given initial condition in phase space. In particular, Noid *et. al.* showed analytically [4] that the third-order nonlinear response function $R_c^{(3)}(t, 0, t)$ of thermally distributed Morse oscillators grows linearly with time. However, the third-order response functions $R_c^{(3)}(t_3 = \text{const}, 0, t_1)$ and $R_c^{(3)}(t_3, 0, t_1 = \text{const})$ were found to converge for the thermally distributed Morse [4] and quartic [2] oscillators, respectively. In this Letter we generalize the above results to all systems with quasiperiodic dynamics and show that there always exists a direction in $(t_n, \ldots, t_1)$ space along which the nonlinear response function $R_c^{(n)}(t_n, \ldots, t_1)$ diverges and no smooth distribution function of phase-space initial conditions can remove this divergence.

Regular dynamics allow simple analytical description and have a convenient representation in action-angle variables [6–9]. Making use of the quasiperiodicity, we expand a dynamic function $\alpha(t)$ in Fourier series [6] $\alpha(t) = \sum_{\mathbf{n}} \alpha_{\mathbf{n}} e^{\iota \mathbf{n} \varphi}$, where $\boldsymbol{\varphi} = \boldsymbol{\omega} t + \boldsymbol{\varphi}_0$ are angle variables and $\boldsymbol{\omega}(\mathbf{J})$, $\alpha_{\mathbf{n}}(\mathbf{J})$ are functions of actions $\mathbf{J}$ only. For the purpose of simplicity, we consider one-dimensional systems. The discussion can be easily extended to a system with an arbitrary number of degrees of freedom, replacing scalars with vectors. Substituting a one-dimensional form of Fourier series into the expression (2) for the classical response function and using the identity $Tr[\{A, B\}C] = \mathrm{Tr}[A\{B, C\}]$, we get the following results for the three lowest order response functions

$$R_c^{(1)}(t) = -\mathrm{Tr}[\alpha(t)\{\alpha(0), \rho\}] = -\sum_{n,k} \int dJ \alpha_n e^{\iota n\omega t} \int d\varphi_0 F_k(J, \varphi_0) e^{\iota(n+k)\varphi_0} \tag{3}$$

$$\begin{aligned} R_c^{(2)}(t_2, t_1) &= \mathrm{Tr}(\{\alpha(t_2+t_1), \alpha(t_1)\}\{\alpha(0), \rho\}) \\ &= \sum_{n,m,k} \int dJ e^{\iota(n+m)\omega t_1 + \iota n\omega t_2} \left\{ \iota\left(\alpha_n n \frac{\partial \alpha_m}{\partial J} - \alpha_m m \frac{\partial \alpha_n}{\partial J}\right) + t_2 mn\alpha_n\alpha_m \frac{\partial \omega}{\partial J} \right\} \int d\varphi_0 F_k(J, \varphi_0) e^{\iota(n+m+k)\varphi_0} \end{aligned} \tag{4}$$

$$\begin{aligned} R_c^{(3)}(t_3, 0, t_1) &= -\mathrm{Tr}(\{\alpha(t_3+t_1), \alpha(t_1)\}\{\alpha(t_1), \{\alpha(0), \rho\}\}) \\ &= -\sum_{n,m,k,l} \int dJ e^{\iota(n+m+l)\omega t_1 + \iota n\omega t_3} \left\{ \iota\left(\alpha_n n \frac{\partial \alpha_m}{\partial J} - \alpha_m m \frac{\partial \alpha_n}{\partial J}\right) + t_3 mn\alpha_n\alpha_m \frac{\partial \omega}{\partial J} \right\} \int d\varphi_0 e^{\iota(n+m+l+k)\varphi_0} \\ &\quad \times \left\{ \iota\alpha_l l \frac{\partial F_k}{\partial J} - \left(\frac{\partial \alpha_l}{\partial J} + \iota t_1 l\alpha_l \frac{\partial \omega}{\partial J}\right)\left(\frac{\partial F_k}{\partial \varphi_0} + \iota k F_k\right) \right\}, \end{aligned} \tag{5}$$

where $F_k(J, \varphi_0) = \iota\alpha_k k \frac{\partial \rho}{\partial J} - \frac{\partial \alpha_k}{\partial J} \frac{\partial \rho}{\partial \varphi_0}$. Classical expressions for nonlinear response functions (4) and (5) contain terms with time-dependent preexponential factors that can diverge at long times. Below we prove that nonlinear response functions indeed diverge at $t_n \to \infty$ and no phase-space distribution density can remove the divergence. Obviously, the presence of these terms in the above expressions is a consequence of the anharmonicity $\frac{\partial \omega}{\partial J} \neq 0$ whereas harmonic systems $\frac{\partial \omega}{\partial J} \equiv 0$ do not encounter any difficulties in application of classical response theory [4] (it should mentioned that for a completely harmonic system, nonlinear response functions treated here are identically zero if the dipole moment depends linearly on position). In the rest of the present Letter we assume that the system is anharmonic and does not have stationary points $\frac{\partial \omega}{\partial J} = 0$.

We start with the linear response function (3). After the integration over φ_0 is carried out, the expression for $R_c^{(1)}(t)$ takes the form

$$R_c^{(1)}(t) = -\sum_{n,k} \int f_{nk}(J) e^{\iota n\omega t} dJ. \tag{6}$$

The integrals in Eq. (6) have a form of the Fourier integral $G(t) = \int_a^b f(x) e^{\iota t S(x)} dx$, which has well-known asymptotic decompositions at large values of parameter t. For physical applications, the interval $[a, b]$ can always be chosen to be finite and the distribution density $\rho(J, \varphi)$, potential surface $U[r(J, \varphi)]$, and anharmonic frequency $\omega(J)$ are usually smooth functions (2 times continuously differentiable functions at least). Thus, the following asymptotic decomposition at large values of parameter t is valid

$$G(t) = \frac{f(b)}{\iota t S'(b)} e^{\iota t S(b)} - \frac{f(a)}{\iota t S'(a)} e^{\iota t S(a)} + O(t^{-2}) \tag{7}$$

which for the linear response function (6) results in

$$R_c^{(1)}(t) = \frac{1}{t} \sum_{nk} (C_{nk}^{(1)} e^{\iota n\omega_1 t} + C_{nk}^{(2)} e^{\iota n\omega_2 t}) + O(t^{-2}), \tag{8}$$

where $C_{nk}^{(1)}$, $C_{nk}^{(2)}$, ω_1, and ω_2 are constants. From Eq. (8) one can see that the linear response function decays to zero as $O(1/t)$ or faster for *any* smooth phase-space distribution density ρ. The latter justifies the convergence of the linear response function for thermal distributions $\rho = \frac{1}{Z} e^{-\beta H}$ [2]. The direct application of Eq. (7) to the Morse potential with thermal distribution results in the asymptotic behavior shown in Fig. 1. The exact numerical calculation agrees with the asymptotic expression (8) at long times.

Next, we examine the behavior of the classical second-order response function (4). Integrating out φ_0 the expression (4) can be written in the following form

$$\begin{aligned} R_c^{(2)}(t_2, t_1) &= \sum_{n,m,k} \int f_{nmk}(J) e^{\iota(n+m)\omega t_1 + \iota n\omega t_2} dJ \\ &\quad + t_2 \sum_{n\neq 0, m\neq 0, k} \int g_{nmk}(J) e^{\iota(n+m)\omega t_1 + \iota n\omega t_2} dJ. \end{aligned} \tag{9}$$

The first term in Eq. (9) will converge at large t_1 and t_2 similar to the linear response function discussed previ-

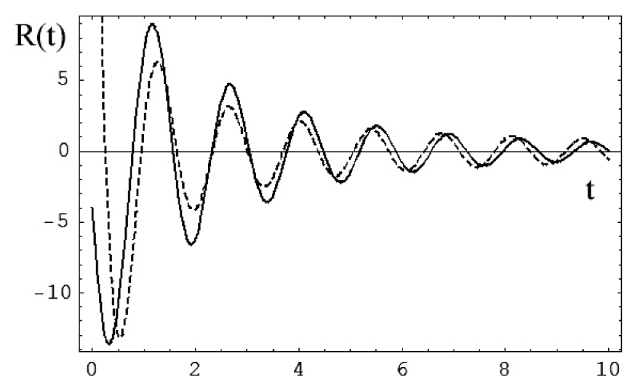

FIG. 1. The linear response function for the $1D$ Morse oscillator with the dipole moment $\alpha = x$. The solid line represents the exact calculation with the classical formula (3); the dashed line corresponds to the first asymptotic term $O(1/t)$ from Eq. (8).

ously. The problem is the second term. Different from the linear response function, the expression for the second-order response function has directions in (t_1, t_2) plane, along which the power of the exponent in (9) is zero or time independent. These directions are defined by

$$(n + m)t_1 + nt_2 = C, \tag{10}$$

and obviously depend on the type of polarization function $\alpha(t)$ in the way that a particular polarization function has particular spectral components α_k and thus a particular set of values of n and m. We now consider one of these directions by fixing n and m at values n^* and m^*, and assume that $n^* \neq 0$, then $t_2 = -(\frac{n^*+m^*}{n^*})t_1 + \frac{C}{n^*}$. Along this direction the second-order response function (9) becomes

$$R_c^{(2)}(t_2(t_1), t_1) = \sum_{n,m,k} \int dJ (f_{nmk}(J) + \frac{C}{n^*} g_{nmk}(J)) e^{\iota(1/n^*)(mn^* - nm^*)\omega t_1 + \iota(n/n^*)\omega C} - \left(\frac{n^* + m^*}{n^*}\right) t_1 \sum_{n,m,k} \int dJ g_{nmk}(J) e^{\iota(1/n^*)(mn^* - nm^*)\omega t_1 + \iota(n/n^*)\omega C}, \tag{11}$$

where C is a constant from the expression (10). In summation over n and m in Eq. (11), all the integrals with $(mn^* - nm^*) \neq 0$ in the exponent will decay as $O(1/t_1)$ or faster, as discussed for the linear response function, and thus the first part of the expression (11) will decay at $t_1 \to \infty$, while the second part will remain bounded $O(1)$. Yet, the integrals with $(mn^* - nm^*) = 0$ result in the linear divergence $O(t_1)$ of the second term in the expression (11). There will be at least one such term ($n = n^*$, $m = m^*$) in the summation over n and m while all such terms must satisfy the condition $m/n = m^*/n^*$. Taking the above arguments into account, the expression (11) at large t_1 behaves as

$$R_c^{(2)}(t_2(t_1), t_1) \sim t_1 \int dJ \sum_{(m/n)=(m^*/n^*)} \tilde{g}_{nm}(J) e^{\iota(n/n^*)\omega C}. \tag{12}$$

The case when the summation in Eq. (12) can be exactly zero is when $\tilde{g}_{-n,-m} = -\tilde{g}_{n,m}$ and $C = 0$. Yet if $C \neq 0$, the right side of the expression (12) does not disappear. Then there exist infinitely many lines $(n + m)t_1 + nt_2 = C$ in (t_1, t_2) plane, along which the second-order classical response function diverges in a nonoscillatory manner as $O(t_1)$ and there is *no* smooth phase-space distribution function that can remove this divergence. One should also note that $R_c^{(2)}(t_2 = \text{const}, t_1)$ and $R_c^{(2)}(t_2, t_1 = \text{const})$ are bounded, as follows directly from Eq. (9) using decomposition (7).

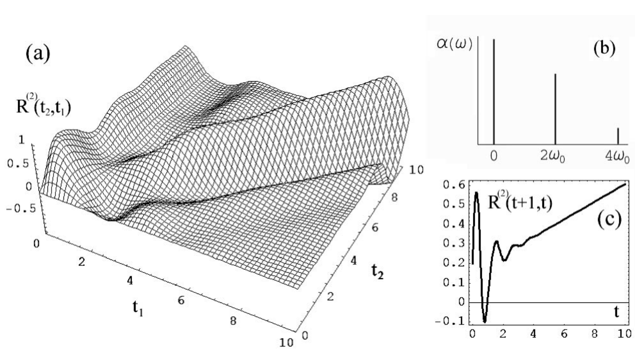

FIG. 2. The second-order classical response function for the 1D Morse oscillator with the fourth-order polarization $\alpha = (b + b^+)^4$ is shown in (a). The spectrum of $\alpha(t)$ is presented in the top right corner (b), where ω_0 is the fundamental frequency. The behavior of the classical second-order response function along the direction $t_2 = t_1 + 1$ is shown in the inset (c).

The numerical examples of the classical second-order response function are shown in Fig. 2 for the thermally distributed Morse and in Fig. 3 quartic oscillators. The obvious difference of the divergent behavior in both figures comes from the fact that polarizations $\alpha(t)$ have different spectral components as shown in Figs. 2(b) and 3(b). Thus, the direction of the most intensive divergence is $t_1 - t_2 = C_1$ in Fig. 2(b) for the Morse oscillator with polarization $\alpha = (b + b^\dagger)^4$ [3] and $2t_1 - t_2 = C_2$ in Fig. 3(b) for the quartic oscillator with polarization $\alpha = x$.

The same line of reasoning can be applied to analyze the behavior of the classical third-order response function $R^{(3)}(t_3, 0, t_1)$. Rewriting Eq. (5) in the form

$$\begin{aligned} R_c^{(3)}(t_3, 0, t_1) = &\sum_{n,m,k,l} \int b_{nmkl}(J) e^{\iota(n+m+l)\omega t_1 + \iota n\omega t_3} dJ \\ &+ t_1 \sum_{n,m,k,l} \int f_{nmkl}(J) e^{\iota(n+m+l)\omega t_1 + \iota n\omega t_3} dJ \\ &+ t_3 \sum_{n,m,k,l} \int g_{nmkl}(J) e^{\iota(n+m+l)\omega t_1 + \iota n\omega t_3} dJ \\ &+ t_1 t_3 \sum_{n,m,k,l} \int h_{nmkl}(J) e^{\iota(n+m+l)\omega t_1 + \iota n\omega t_3} dJ, \end{aligned} \tag{13}$$

the directions $(n + m + l)t_1 + nt_3 = C, C \neq 0$ result in nonoscillatory quadratic divergence $O(t_1^2)$ of $R^{(3)}(t_3(t_1), 0, t_1)$ for *any* smooth phase-space distribution density. Again, using the decomposition (7) one can see that $R_c^{(3)}(t_3, 0, t_1 = \text{const})$ and $R_c^{(3)}(t_3 = \text{const}, 0, t_1)$ are bounded functions of time. The latter agrees with the results reported in Refs. [2,4] for the quartic and Morse potentials.

The numerical results for $R^{(3)}(t_3, 0, t_1)$ are presented in Fig. 4 for the system of thermally distributed quartic oscillators. The numerical calculations observe the linear divergence along the diagonal $t_1 = t_3 = t$ due to the smallness of the quadratic terms $O(t_1^2)$ along the directions

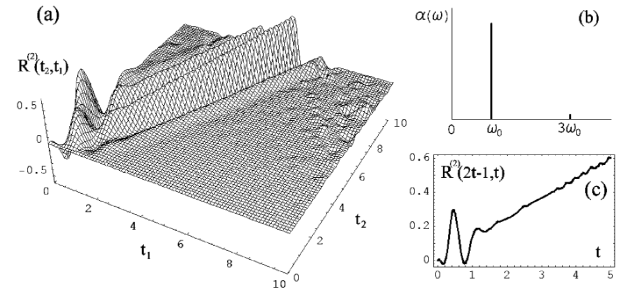

FIG. 3. The second-order classical response function for the $1D$ quartic oscillator with polarization $\alpha = x$ is shown in (a). The typical spectrum of $\alpha(t)$ is presented in the top right corner (b), where ω_0 is the fundamental frequency. The behavior of the classical second-order response function along the direction $t_2 = 2t_1 - 1$ is shown in the inset (c).

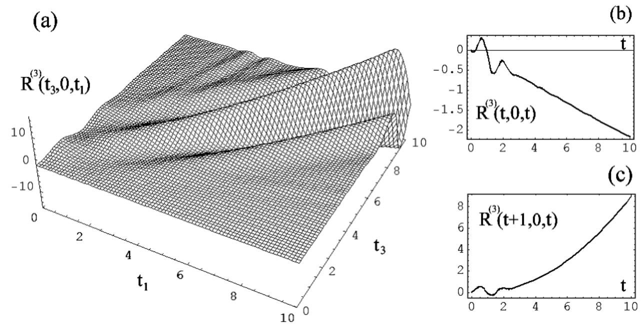

FIG. 4. The third-order classical response function $R^{(3)}(t_3, 0, t_1)$ for the $1D$ quartic oscillator with polarization $\alpha = x$ is shown in (a). The linear divergent behavior of $R^{(3)}(t, 0, t)$ is shown in the inset (b) with the quadratic divergence of $R^{(3)}(t_3, 0, t_1)$ along the direction $t_3 = t_1 + 1$ presented in the inset (c).

$(n + m + l)t_1 + nt_3 = 0$ within the length of the numerical calculation. The same divergence was observed in [4] for the thermally distributed Morse oscillators. The low temperature approximation $\beta D \gg 1$ used in [4] means that the motion of the system takes place in nearly harmonic region, resulting in almost a single spectral component $|\alpha_1|$ of $\alpha(t) = x(t)$ [like that in Fig. 3(b)]. Thus the term, quadratic in time, is exactly zero as it follows from Eq. (5)

$$R_c^{(3)}(t, 0, t) \simeq t \int \left(\sum_{n=\pm 1} n^4 |\alpha_n|^4 \right) \frac{\partial \omega}{\partial J} \frac{\partial^2 \rho}{\partial J^2} dJ - t^2 \int \left(\sum_{n=\pm 1} n^5 |\alpha_n|^4 \right) \iota \left(\frac{\partial \omega}{\partial J} \right)^2 \frac{\partial \rho}{\partial J} dJ. \quad (14)$$

It is possible now to generalize the discussion to the nth order response function. Substituting Fourier decompositions of $\alpha(t)$ into the expression for the classical response function $R_c^{(n)}(t_n, \ldots, t_1)$, one obtains the terms containing exponents $e^{\iota\omega(k_1 t_1 + \cdots + k_n t_n)}$ with the time-dependent prefactors $t_1^\alpha t_2^\beta \ldots t_n^\delta$, $\alpha + \beta + \cdots + \delta \leq n - 1$. These terms diverge in time as $O(t_1^\alpha t_2^\beta \ldots t_n^\delta)$ on the plane $k_1^* t_1 + \cdots + k_n^* t_n = \text{const}$ in $(t_1, \ldots, t_n)$ space. In particular, the direction $t_n = C_n, t_{n-1} = C_{n-1}, \ldots, t_3 = C_3, k_2^* t_2 + k_1^* t_1 = C$ allows the same range of discussions as for $R^{(2)}(t_2(t_1), t_1)$ and $R^{(3)}(t, 0, t)$ stated above, showing that no phase-space distribution function can remove the divergence of $R^{(n)}(C_n, \ldots, C_3, (C - k_1^* t_1)/k_2^*, t_1)$ along this direction.

In the present Letter we have studied the divergent behavior of the classical response function for a system with regular dynamics and demonstrated that no smooth phase-space distribution function of the initial conditions can remove the divergence of the classical nonlinear response function for quasiperiodic systems. Our analysis generalizes the analytical and numerical results obtained earlier for Morse and cubic oscillators [2–4]. It shows the conceptual difficulty of taking the classical limit of the quantum response theory because the quantum nonlinear response function is finite and the classical nonlinear response function diverges for systems with regular dynamics. One possible reason was pointed out by van Kampen [1], who argued the validity of the application of classical time-dependent perturbation theory. Another reason resides in the fact that, while both infinite quantum mechanical and classical perturbation series represent the same physical quantity, which is polarization $P(t)$, individual expansion terms are not necessarily equivalent. In contrast to the quasiperiodic motion, the chaotic and dissipative dynamics [5,10–13] appear to observe the convergence of the classical response functions. The correspondence of the classical limit with the quantum and experimental quantities remains a challenge and is a subject for future study.

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