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The influence of dissipation on the quantum-classical correspondence: Stability of stochastic trajectories

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The quantum-classical correspondence in the presence of dissipation is studied. The semiclassical expression for the linear response function of an anharmonic system is expressed in a series containing classical stability matrix elements, which can diverge due to the chaotic behavior of stochastic trajectories. The presence of dissipation in most cases removes the divergence of higher-order correction terms, thus suppressing quantum effects and making the system more classical. The regime of system-bath coupling, which makes quantum dynamics completely classical, is obtained in terms of friction, temperature, and anharmonicity. Special cases when bath coupling may lead to enhancement of quantum effects are discussed. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3154142]

I. INTRODUCTION

The concept of quantum-classical correspondence for isolated systems has been extensively discussed in literature.[1–7] However, all real systems are open and subject to the influence of noise from the surroundings. The influence of noise is especially important in chemistry, where the coupling between molecular systems and thermal bath is responsible for fluctuations in the structure and energy levels of the molecule, the flow of energy into and out of the molecule, and thermally activated rate processes.

Coupling of quantum systems to the surroundings results in the loss of quantum coherence.[8,9] Many theoretical and experimental works demonstrated that decoherence plays an essential role in quantum-classical correspondence and that in the presence of decoherence the quantum dynamics behaves more classically than in the absence of decoherence.[10–15] This suggests that the agreement between the quantum and classical response functions will improve if the coupling to the bath is introduced. However, in some cases, it was shown that dissipation enhances quantum effects.[16,17] It is thus interesting to find the range of parameters of dissipative environment that can reduce quantum effects and, above some threshold, even make the system of interest classical.

Semiclassical analysis is a promising tool for the analytical study of the environmental effects on a quantum system. In recent papers[7,18] we proposed a semiclassical expression for the quantum response and correlation functions in the form of semiclassical corrections to the classical expressions of response and correlation functions. The proposed semiclassical series provided exact quantum results for the simple anharmonic potentials such as Morse potential[7] and infinite square well potential.[18] The quantum coherent effects are reconstructed in this semiclassical approach due to the dependence of the correction terms on the classical stability matrix elements. For instance, the semiclassical expression for the linear response function[19] of a canonically distributed noninteracting integrable systems[20] reads

$$R(t) = \sum_n R_n(t) e^{-\beta E(J_n)}, \tag{1.1}$$

with microcanonical response function $R_n(t)$ in the form[7]

$$\begin{aligned} R_n(t) = &- \int \{\alpha(t), \alpha(0)\} \frac{\delta(J - J_n)}{2\pi} dJ d\varphi_0 \\ &+ \frac{\hbar^2}{24} \int (\alpha(t) \hat{D}^3 \alpha(0)) \frac{\delta(J - J_n)}{2\pi} dJ d\varphi_0 \\ &- \frac{\hbar^4}{1920} \int (\alpha(t) \hat{D}^5 \alpha(0)) \frac{\delta(J - J_n)}{2\pi} dJ d\varphi_0 + \cdots, \end{aligned} \tag{1.2}$$

where the first term is the classical microcanonical response function, $\{\cdots\}$ is a Poisson bracket, $\alpha(t)$ is a classical dipole moment, and $\hat{D} = ((\overleftarrow{\partial}/\partial\varphi_0)(\vec{\partial}/\partial J) - (\overleftarrow{\partial}/\partial J)(\vec{\partial}/\partial\varphi_0))$ is a differential operator over the classical action-angle variables $\{J, \varphi_0\}$. The correction terms with coefficients $\hbar^n$ contain classical stability derivatives $\partial^n \alpha(t)/\partial J^n \sim \partial^n x(t)/\partial x(0)^m \partial p(0)^{n-m}$, which reflect the coherence between the $n+1$ classical trajectories. Quantum coherence is therefore transformed into the stability of the nearby classical trajectories. Resummation of all correction terms recovers the quantum expression of the response function. One can notice that the quantum coherent effects reside entirely in the semiclassical terms $\sim\hbar^n$. If for some reason the magnitude of these terms is small so that these terms can be neglected (normally they diverge with time) then the quantum effects can be neglected as well.

It is straightforward to extend this approach to dissipative classical dynamics and to study dissipation effects on the quantum coherence by means of decoherence of classical trajectories (stability matrix elements). The idea of using classical Langevin trajectories in semiclassical calculations

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of the dynamics of quantum systems coupled to harmonic bath was also developed in Refs. 21 and 22. It was shown[22] that in the continuum limit of the semiclassical initial value representation, the path integral over system paths includes only classical Langevin paths.

Due to the simplicity of the form of semiclassical corrections, which are just functions of stability derivatives, it is relatively easy to study dissipation effects on quantum-classical correspondence; when these corrections become small the effects of quantum coherence are negligible. In this paper we study the effect of noise from environment on the temporal behavior of the system's stability matrix elements and consider the following question: At what temperature and friction can the divergence of stability matrices be removed so that higher order semiclassical correction terms can be omitted?

The paper is organized as follows. In Sec. II we describe the harmonic bath model and derive the equations of motion for the stability matrix elements. In Sec. III we study the stability of the matrix elements for an isolated system. In Sec. IV we discuss the stability of matrix elements in the presence of nonresonant bath. In Sec. V we study the stability of matrix elements in resonant bath. The dynamic behavior of higher order stability matrices in the presence of dephasing is generalized in Sec. VI with numerical results provided in Sec. VII. The results obtained are discussed in Sec. VIII.

II. GLE AND ITS STABILITY MATRIX

A. Model of dissipative system

Dissipative systems are often defined as systems coupled linearly to a harmonic bath.[23] The classical dynamics of these systems is described by the generalized Langevin equation (GLE), which is obtained as the continuum limit of an infinite number of bath oscillators. In this limit, the bath degrees of freedom are collectively accounted for by the addition of friction and random force terms to the Newton's equations of motion of the system of interest.[23] GLE is a convenient analytical tool for describing dissipation effects. Here we consider an anharmonic system with potential $V(q)$ linearly coupled to a harmonic bath. The system-bath Hamiltonian has the following form:

$$H = \frac{p^2}{2\mu} + V(q) + \frac{1}{2}\sum_{j=1}^{N}\left(p_j^2 + \omega_j^2\left(x_j - \frac{c_j}{\omega_j^2}q\right)^2\right), \tag{2.1}$$

where ω_j is a bath mode harmonic frequency and c_j is a coupling strength. The equation of motion for the system coordinate q takes the GLE form,[23]

$$\mu\ddot{q} + \frac{dV(q)}{dq} + \mu\int_0^t dt'\,\gamma(t-t')\dot{q}(t) = \xi(t), \tag{2.2}$$

with the friction kernel,

$$\gamma(t) = \frac{1}{\mu}\sum_{j=1}^{N}\frac{c_j^2}{\omega_j^2}\cos(\omega_j t), \tag{2.3}$$

and random force

$$\xi(t) = \sum_{j=1}^{N} c_j\left(\left(x_j - \frac{c_j}{\omega_j^2}q(0)\right)\cos(\omega_j t) + \frac{p_j}{\omega_j}\sin(\omega_j t)\right). \tag{2.4}$$

The friction kernel is related to the correlation function of random force via the fluctuation-dissipation theorem,

$$\langle\xi(t)\xi(t')\rangle = \mu kT\gamma(t-t'), \tag{2.5}$$

where T is a temperature of the bath. We take the spectral density of a harmonic bath to be of the Ohmic form with the cutoff frequency ω_c,[14]

$$J_0(\omega) = \mu\gamma_0\omega e^{-\omega/\omega_c}. \tag{2.6}$$

This spectral density results in a friction kernel of the form

$$\gamma(t) = \frac{2\gamma_0}{\pi}\frac{\omega_c}{1+t^2\omega_c^2}, \tag{2.7}$$

which becomes a delta function as $\omega_c \to \infty$. In this paper, we vary ω_c with respect to the frequency of the system ω_s to cover both the resonant case ($\omega_c > \omega_s$), which allows energy transfer between the system and the bath, and nonresonant case ($\omega_c \ll \omega_s$), which does not allow energy transfer.

B. Time evolution of stability matrix elements

The time evolution of the stability matrix elements can be obtained from the Langevin Eq. (2.2),

$$\frac{dq}{dt} = \frac{p}{\mu},$$

$$\frac{dp}{dt} = -\left.\frac{\partial V}{\partial q}\right|_{q=q(t)} - \int_0^t dt'\,\gamma(t-t')p(t') + \xi(t). \tag{2.8}$$

Considering initial conditions $q(0)$ and $p(0)$ as variables, we take partial derivative of the Eq. (2.8), with respect to $q(0)$ and $p(0)$, and obtain the equations for the first order stability matrix elements $M_q^q = \partial q(t)/\partial q(0)$, $M_q^p = \partial p(t)/\partial q(0)$, $M_p^q = \partial q(t)/\partial p(0)$, and $M_p^p = \partial p(t)/\partial p(0)$,

$$\frac{d}{dt}M_q^q = M_q^p,$$

$$\frac{d}{dt}M_q^p = -V''(q)M_q^q - \int_0^t dt'\,\gamma(t-t')M_q^p(t) - \gamma(t),$$

$$\frac{d}{dt}M_p^q = M_p^p, \tag{2.9}$$

$$\frac{d}{dt}M_p^p = -V''(q)M_p^q - \int_0^t dt'\,\gamma(t-t')M_p^p(t),$$

where $V''(q) \equiv \partial^2 V/\partial q^2$. The derivatives $\partial\xi(t)/\partial q(0)$ and $\partial\xi(t)/\partial p(0)$ are found by performing differentiation with respect to $q(0)$ and $p(0)$ of the expression (2.8) before taking the continuum limit of an infinite number of bath oscillators,[23] i.e.,

$$\frac{\partial \xi(t)}{\partial q(0)} = \frac{\partial}{\partial q(0)} \sum_{j=1}^{N} c_j \left(\left(x_j - \frac{c_j}{\omega_j^2} q(0) \right) \cos(\omega_j t) + \frac{p_j}{\omega_j} \sin(\omega_j t) \right) = - \sum_{j=1}^{N} \frac{c_j^2}{\omega_j^2} \cos(\omega_j t) = - \gamma(t),$$

$$\frac{\partial \xi(t)}{\partial p(0)} = \frac{\partial}{\partial p(0)} \sum_{j=1}^{N} c_j \left(\left(x_j - \frac{c_j}{\omega_j^2} q(0) \right) \cos(\omega_j t) + \frac{p_j}{\omega_j} \sin(\omega_j t) \right) = 0. \tag{2.10}$$

Considering Eq. (2.9) one notices that, different from the original equations of motion (2.8), Eq. (2.9) does not have explicit stochastic terms. The only source of stochasticity comes through the stochastic behavior of $q(t)$, which is contained in the anharmonic terms of $V(q)$, i.e., in the derivative $V''(q)$ (thus, for instance, for a harmonic potential, Eq. (2.9) is analytical and does not contain any source of stochastisity). It is thus expected that the effect of thermal fluctuations on the propagation of stability matrices is smaller for systems with lower anharmonicities. Since the propagation of stability matrix elements explicitly influences the dynamic behavior of quantum corrections, which are responsible for quantum coherent effects,[7,18] we expect that the temperature effects on quantum decoherence will be smaller for systems with lower anharmonicity.

C. Markovian limit

Equation (2.9) can be simplified for further analytical derivations under the Markovian approximation[24] to the friction kernel in the original Langevin Eq. (2.2), $\int_0^t dt' \gamma(t-t')\dot{q}(t') \approx \gamma'(\omega_s)\dot{q}(t)$. The Markovian approximation indicates that the energy loss occurs only when the resonance condition is satisfied, i.e., there is a bath mode that has the same frequency as the system's frequency of oscillations ω_s. Here $\gamma'(\omega)$ is the real part of the Fourier transform of the friction kernel, which for the Ohmic friction kernel Eq. (2.7) reads

$$\gamma'(\omega) = \gamma_0 e^{-\omega/\omega_c}. \tag{2.11}$$

We thus obtain from Eq. (2.9)

$$\ddot{M}_q^q + \gamma'(\omega_s)\dot{M}_q^q + V''(q)M_q^q = - \gamma(t),$$

$$\ddot{M}_p^q + \gamma'(\omega_s)\dot{M}_p^q + V''(q)M_p^q = 0, \tag{2.12}$$

where $\gamma(t)$ is a fast decaying function. Therefore, to study the stability of the solutions of the above equations, it is sufficient to study the stability of the following equation:

$$\ddot{M} + \gamma'(\omega_s)\dot{M} + V''(q)M = 0, \tag{2.13}$$

which is an equation of motion for the damped harmonic oscillator with the modulated frequency. For the harmonic potential $V(q)$, the solution of the equation is a simple harmonic oscillation with the decaying amplitude if $\gamma'(\omega_s) \neq 0$. If $V(q)$ is anharmonic with the cubic anharmonicity ε, $V(q) = (\omega_0^2 q^2/2) + \varepsilon q^3/3$, then Eq. (2.13) reads

$$\ddot{M} + \gamma'(\omega_s)\dot{M} + \omega_0^2 M = 2\varepsilon q(t) M. \tag{2.14}$$

The term $2\varepsilon q(t)M$ acts as a driving force to harmonic oscillations resulting in parametric resonance at Fourier components of $q(t)$ at frequencies $2\omega_0$ and ω_0,[25] which can lead to the divergence of solution $M(t)$. The unbound growth of stability derivatives M_i^j in time is therefore entirely due to the anharmonicity of the system's potential. However, both damping term $\gamma'(\omega_s)\dot{M}$ and fluctuations of $q(t)$ can reduce this divergence. We will study the stability of Eq. (2.13) in detail in the following subsections.

III. THE DIVERGENCE OF STABILITY MATRIX ELEMENTS OF AN ISOLATED SYSTEM

If the system is not coupled to the environment, Eq. (2.13) reads

$$\ddot{M} + V''(q)M = 0, \tag{3.1}$$

where $V(q(t))$ is a periodic function for systems with regular dynamics. Equation (3.1) is of the type of Hill's equation and the stability of its solutions can be analyzed by means of Hill's matrix.[26] To write down Hill's matrix we need to specify a particular form of potential $V(q)$. In this paper we consider a simple analytically solvable anharmonic potential with harmonic frequency $\omega_0 = 1$,

$$V(q) = \frac{q^2}{2} + \frac{\varepsilon q^3}{3}. \tag{3.2}$$

The cubic potential represents the first two terms of Taylor expansion of the Morse potential and is widely used in literature for the analysis of the effects of anharmonicity.[24,27]

The analytical solution for the motion in potential (3.2) is known,[28]

$$q(t) = q(0) + a\,\mathrm{sn}^2(\omega t, k^2), \quad \dot{q}(0) = 0, \tag{3.3}$$

where $\mathrm{sn}(u,k^2)$ is the Jacobian elliptic sine function and

$$P = \varepsilon q(0), \tag{3.4}$$

$$k = \sqrt{\frac{1}{2} + \frac{3(2P^2 + 2P - 1)}{3 + (1+2P)\sqrt{3(1-2P)(3+2P)}}}, \tag{3.5}$$

$$\omega = \frac{1}{2}\sqrt{\frac{1}{2} + P + \frac{1}{6}\sqrt{3(1-2P)(3+2P)}}, \tag{3.6}$$

$$a = \frac{-12P(1+P)}{\varepsilon(\sqrt{3(1-2P)(3+2P)} + 3(1+2P))}. \tag{3.7}$$

To write down the Fourier expansion of $V''(q(t)) = 1 + 2\varepsilon q(t)$, we use the cosine expansion of the Jacobian sine function,[29]

$$\mathrm{sn}^2(\omega t, k^2) = \frac{K - E}{Kk^2} - \frac{2\pi^2}{K^2 k^2} \sum_{n=1}^{\infty} \frac{nQ^n}{1 - Q^{2n}} \cos(n\pi\omega t/K), \tag{3.8}$$

where $K(k)$ and $E(k)$ are the complete elliptic integrals of the first and second kind, respectively, k is the modulus, $k' = \sqrt{1-k^2}$ is the complementary modulus of the elliptic func-

tions, $Q=\exp(-\pi K'/K)$, and $K'\equiv K(k')$. The Fourier expansion of $V''(q(t))$ is therefore

$$V''(q(t)) = \sum_{n=-\infty}^{\infty} v_n e^{i\pi\omega nt/K}, \tag{3.9}$$

where

$$v_0 = 1 + 2q(0)\varepsilon + 2a\varepsilon\left(\frac{K-E}{Kk^2}\right),$$
$$v_n = -\frac{4a\varepsilon\pi^2}{K^2k^2}\frac{nQ^n}{2(1-Q^{2n})}. \tag{3.10}$$

Hill's matrix, which is needed to study the stability of Eq. (3.1), reads[26]

$$D_{nm} = \frac{v_{n-m}}{v_0 - (\omega\pi n/K)^2} + \delta_{n,m}, \tag{3.11}$$

where $\delta_{n,m}$ is a Kronecker symbol, $v_{n-m}=0$ at $n=m$ and n,m go from $-\infty$ to ∞. The solution to Eq. (3.1) is stable (nondivergent) if $\Delta\equiv|1-2\sin^2(K\sqrt{v_0})\det(D_{nm})|<1$ and exponentially diverges if $\Delta>1$. The numerical calculation of $\det(D_{nm})$ using Eq. (3.11) shows that $D_{nm}\to 0$ as $|n|,|m|\to\infty$. For $\epsilon=0.5$ and $q(0)=0.7$, $\det(D_{nm})$ is already equal to 2×10^{-12} for the 15×15 matrix of D_{nm}. This means that for the regular motion, $\Delta=1$ and lies right on the border of stability; it is neither stable nor exponentially divergent. The solution to Eq. (3.1) should be thus linear, which easily turns into exponentially divergent function (since the linear term is the lowest order term of the Taylor series of exponent) if Δ becomes greater than 1 and into bounded function if Δ becomes smaller than 1, see Fig. 1. The linear divergence of stability matrices for regular motion is well known and can be shown in a much simpler way in the action-angle representation.[30]

The key result of the above analysis is that nondissipative regular motion corresponds to the border of stability of Hill's Eq. (3.1), therefore, an external noise is likely to shift the solution of the Hills equation to the region of stability, making its solutions bounded. The latter will make the semiclassical corrections in Eq. (1.2) nondivergent and at some threshold of noise, even negligible, allowing these corrections to be omitted and thus suppressing quantum effects. In a special case, external noise of a particular type can shift the solution for stability derivatives [Eq. (3.1)] to the region of instability, resulting in stronger divergence of stability matrices and therefore enhancing quantum effects. The influence of noise on stability of Eq. (3.1) is studied in the following.

IV. STABILITY OF MATRIX ELEMENTS IN THE PRESENCE OF NONRESONANT NOISE

We now consider a system coupled to the environment. We return to Eq. (2.13) and consider a nonresonant case, i.e., when the cutoff frequency ω_c of the bath oscillators is much less than the system's frequency ω_s. Relaxation of $q(t)$ in this case occurs only due to the pure dephasing mechanism. In this case, $\gamma'(\omega_s)=0$ and Eq. (2.13) has now the form similar to Eq. (3.1),

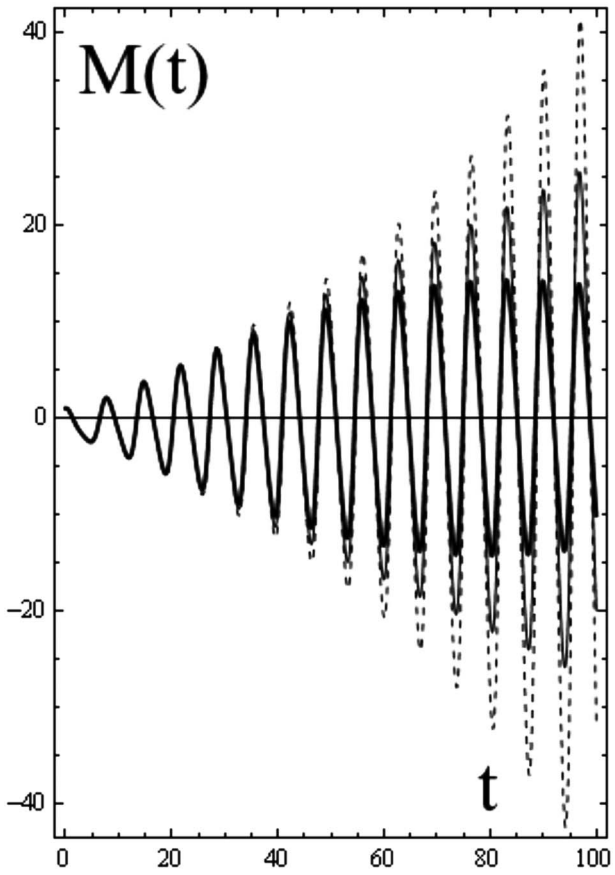

FIG. 1. Solutions of Hill's equations for the different values of stability parameter Δ. The dashed line stands for $\Delta=1.01$, the solid thin line stands for $\Delta=1$, and the solid thick line stands for $\Delta=0.99$.

$$\ddot{M} + V''(q)M = 0, \tag{4.1}$$

except that $q(t)$ in $V''(q(t))$ is stochastic and is subjected to the pure dephasing mechanism.

The low frequency bath shifts the frequency of system's oscillations. Such a blue frequency shift is observed experimentally and is proved theoretically by Levin *et al.* in Ref. 27 and Yang *et al.* in Ref. 31 using the GLE. Following their derivation, the blue frequency shift is of the order of

$$\delta\omega_s = \omega_s^{\text{new}} - \omega_s \approx \frac{\gamma_0}{2}\frac{\omega_c}{\omega_s}, \tag{4.2}$$

where ω_s^{new} is a new system frequency and $\omega_c \ll \omega_s$ is the cutoff frequency. We now check how this frequency shift influences the stability of Eq. (4.1). In the presence of frequency shift, Hill's matrix modifies as follows:

$$D_{nm} = \frac{v_{n-m}}{v_0 - \left(\left(\frac{\omega\pi}{K} + \delta\omega_s\right)n\right)^2} + \delta_{n,m}, \tag{4.3}$$

with coefficients v_n the same as in Eq. (3.10). In Fig. 2 we plot the stability parameter $\Delta=|1-2\sin^2(K\sqrt{v_0})\det(D_{nm})|$ as a function of $\delta\omega_s$. As one can see from the figure, for the blueshifts $\delta\omega_s>0$, the stability parameter is less than 1, which makes the solution of Eq. (4.1) stable and bounded. In the sense of semiclassical series (1.2), quantum mechanical effects are reduced in nonresonant bath.

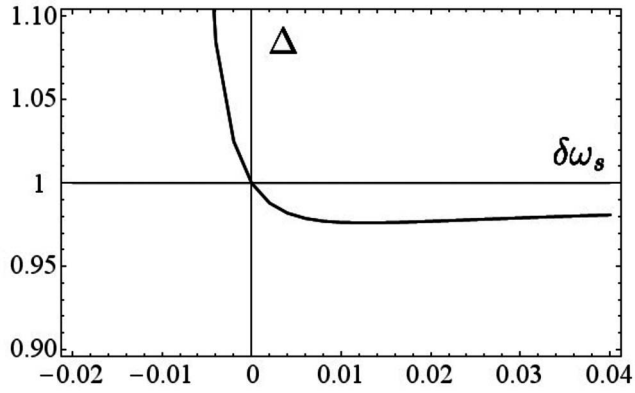

FIG. 2. Dependence of stability parameter Δ on the frequency shift $\delta\omega_s$.

Interestingly, if the effect of coupling to bath introduces a redshift of the system's frequency, i.e., $\delta\omega_s<0$, the semiclassical correction terms would diverge more intensively (see Fig. 2), enhancing quantum effects. The enhancement of quantum effects may be observed for the momentum system-bath coupling, which has opposite effects to the spacial system-bath coupling.[16]

V. STABILITY MATRIX ELEMENTS IN THE PRESENCE OF RESONANT BATH

A. The case of nonzero friction in the absence of thermal noise ($T=0$)

Let us now consider the solution to Eq. (2.13) in the presence of friction ($\omega_c>\omega_s$), but in the absence of noise. In this case $q(t)$ dephases due to energy relaxation. The system's frequency ω_s is usually a slow monotonic function of energy, we can therefore consider $\gamma'(\omega_s)\approx\gamma'(\omega_0)=\gamma'(1)$ to be a constant. Transformation $y=\exp(\gamma'(1)t/2)M(t)$ reduces Eq. (2.13) to

$$\ddot{y}+\left[V''(q)-\frac{\gamma'(1)^2}{4}\right]y=0. \tag{5.1}$$

Since $V''(q(t))=1+2\varepsilon q(t)\to 1$ with $q(t)\sim\exp(-\gamma'(1)t/2)\to 0$, then the solution $y(t)$ becomes a simple harmonic oscillation after the time $1/\gamma'(1)$. Since $y(t)$ is bounded then $M(t)=\exp(-\gamma'(1)t/2)y(t)$ decays exponentially. According to the semiclassical series (1.2), quantum effects are reduced because in the presence of friction the correction terms in Eq. (1.2) decay exponentially rather than diverge with time.

B. Combined effects of friction and thermal noise ($T\neq 0$)

From the above analysis it follows that if only anharmonicity or energy relaxation of system's oscillations $q(t)$ is present, the higher order corrections in semiclassical series (1.2) decay with time and the rate of decay is proportional to the strength of the dephasing rate. However, surprising as it may seem, the simultaneous presence of both anharmonicity and relaxation can lead to exponential divergence of the stability matrices in some cases. We discuss this instability in the present section.

The transformation $y=\exp(\gamma'(\omega_s)t/2)M(t)$ again converts Eq. (2.13) into

$$\ddot{y}+(\tilde{\omega}^2+2\varepsilon q(t))y=0, \tag{5.2}$$

where we replaced $V''(q)$ with its explicit expression and introduced $\tilde{\omega}^2=1-\gamma'(1)^2/4$. This is a well known equation for the Kubo oscillator, in which the harmonic frequency is modulated by the stochastic process $q(t)$. Unfortunately, the theory of stability of Eq. (5.2) is developed only for the case when the correlation time of $q(t)$ is short,[32,33] i.e., very fast dephasing of $q(t)$. The latter is not applicable to the problem under consideration because strong noise from surrounding leads to the fast escape from the cubic potential according to the Kramers mechanism.[34] Indeed, for a particle to stay in the cubic potential one should have temperature that is much lower than the height of the potential barrier, i.e., $T/V_{\max}\ll 1$, which in this case is $V_{\max}=1/6\varepsilon^2$. The border of stability of Eq. (5.2) will be shown below to correspond to $\gamma_0\approx C\varepsilon^2 T$, where $C\sim 1$. This gives the critical value of friction of the order $\gamma_0\ll 1/6$ (in units of $\omega_0=1$), which means slow dephasing rate of the system's oscillations and long correlation time of $q(t)$.

C. Short correlation time of $q(t)$

Let us briefly recall the results of stability analysis of Eq. (5.2) when the correlation time of $q(t)$ is short.[32,33,35,36] In this case, the divergence rate of the second moment of $y(t)$ is given by the exponent[32,33,35,36]

$$\lambda_0=\frac{2\varepsilon^2}{\tilde{\omega}^2}\int_0^\infty(\langle q(t)q(t-t')\rangle-\langle q(t)\rangle^2)\cos(2\tilde{\omega}t')dt'$$

$$=\frac{2\varepsilon^2}{\tilde{\omega}^2}\langle q^2\rangle\int_0^\infty C(t)\cos(2\tilde{\omega}t')dt'=\frac{2\pi\varepsilon^2\hat{C}(2\tilde{\omega})}{\tilde{\omega}^2}\langle q^2\rangle, \tag{5.3}$$

where $C(t)=(\langle q(t)q(t-t')\rangle-\langle q(t)\rangle^2)/\langle q^2\rangle$ is a normalized correlation function and $\hat{C}(\omega)$ is its cosine Fourier transform.

If $\lambda_0>0$ then $\langle y(t)^2\rangle$ diverges as $\exp(\lambda_0 t)$ and the divergence of the original stability matrix element $M(t)$ is then

$$|M(t)|\approx\sqrt{\langle M(t)^2\rangle}\sim e^{(\lambda_0-\gamma'(1))t/2}. \tag{5.4}$$

For converging $M(t)$ we should have $\lambda_0-\gamma'(1)<0$, thus the border of stability corresponds to

$$\lambda_0=\gamma'(1). \tag{5.5}$$

The second moment of $q(t)$ can be found from equipartitioning condition $\langle q^2/2\rangle\approx T/2$ and $\gamma'(1)=\gamma_0 e^{-1/\omega_c}$ from Eq. (2.11). With this and Eq. (5.2) the border of stability (5.5) reads

$$\gamma_0=C'(\tilde{\omega})\varepsilon^2 T, \tag{5.6}$$

where $C'(\omega)=2\pi\hat{C}(2\tilde{\omega})e^{1/\omega_c}/\tilde{\omega}^2$. If γ_0 is lower than that in Eq. (5.6), then stability matrix elements $M(t)$ exponentially diverge; if γ_0 is lower than Eq. (5.6), then $M(t)$ exponentially decays.

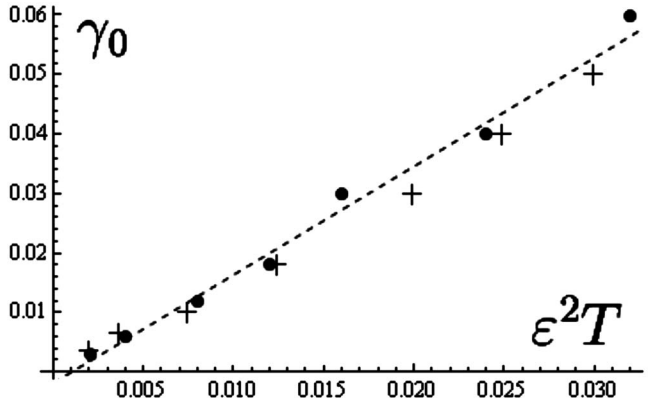

FIG. 3. The boarder of stability of solution $M(t)$ from Eq. (2.13). The region above the line is the region of stability and corresponds to exponentially decaying in time $M(t)$; the region under the line is the region of instability and corresponds to exponentially divergent $M(t)$. Circles denote results for $\varepsilon=0.2$, crosses denote results for $\varepsilon=0.5$. The height of the barrier is $\varepsilon^2 T=0.166$.

D. Long correlation time of $q(t)$

It is interesting now to obtain similar stability criteria [Eq. (5.6)] for the case when the correlation time of $q(t)$ is not short, as in the problem we are dealing with. We obtained these stability criteria numerically. Consider a particle with unit mass in the cubic potential (3.2) coupled to the bath of 400 harmonic oscillators. The cutoff frequency was chosen to be $\omega_c=2\omega_s=2$ and the largest frequency of bath modes was taken to be $\omega_{\max}=5\omega_c=10$. The discretization of bath spectral density [Eq. (2.6)] was made following Ref. 14. We performed calculation of the second moment of $M(t)$ using Eqs. (2.8) and (2.12) for different values of temperature T, friction strength γ_0, and anharmonicity parameter ε, and recorded the step when $\lambda=\lim_{t\to\infty}(\log(\sqrt{\langle M^2(t)\rangle})/t)$ changed its sign. Interestingly, positive λ stands for the largest Lyapunov exponent, which in our case is induced by the dephasing process of the anharmonic one-dimensional motion. The results are shown in Fig. 3. The relation between $\varepsilon^2 T$ and γ_0 in the considered range can be described in a linear form similar to Eq. (5.6), yet with constant coefficient $C'=1.8$,

$$\gamma_0 = C'\varepsilon^2 T. \tag{5.7}$$

From Eq. (5.7), one deduces the general expression for the stability exponent of $|M(t)|$,

$$\lambda = -\frac{\gamma'(1)}{2} + \frac{\lambda_0}{2} = \frac{e^{-1/\omega_c}}{2}(-\gamma_0 + C'\varepsilon^2 T). \tag{5.8}$$

The comparison of this expression with the numerical values of λ is given in Fig. 4 and the parameters of numerical simulations were the same as for Fig. 3. One can confirm the good agreement of expression (5.8) with the numerical calculations.

VI. HIGHER ORDER STABILITY MATRICES

The equations of motion for higher order stability derivatives $\partial^n q(t)/\partial q(0)^k \partial p(0)^{n-k}$ and $\partial^n p(t)/\partial q(0)^k \partial p(0)^{n-k}$ can be obtained similarly as in Eq. (2.9) by subsequent differentiation of Langevin Eq. (2.8) over initial conditions. For instance, for derivative $\partial^2 q(t)/\partial p(0)\partial p(0) \equiv M^q_{pp}(t)$, it follows from Eq. (2.12)

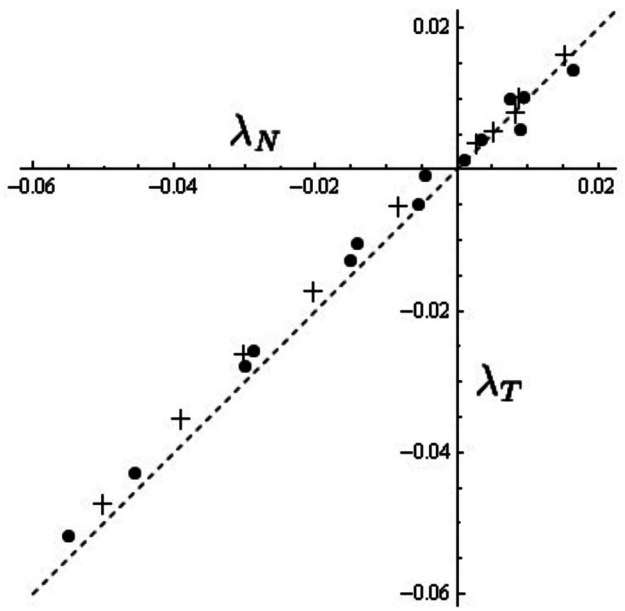

FIG. 4. Stability exponent λ of $|M(t)|$. Vertical axis λ_N stands for numerical value, while horizontal axis λ_T gives the corresponding value from Eq. (5.8). Circles denote results for $\varepsilon=0.2$ and crosses denote results for $\varepsilon=0.5$. The straight line is the line $\lambda_T=\lambda_N$.

$$\ddot{M}^q_{pp} + \gamma'(\omega_s)\dot{M}^q_{pp} + V''(q)M^q_{pp} = -(M^q_p)^2, \tag{6.1}$$

where $V'''(q)=1$ for the cubic potential is used. This is the same equation as Eq. (2.12) except for the driving force. We know that for a driven oscillator, its solution $M^q_{pp}(t)$ is a sum of free oscillations with the appropriate amplitude plus an oscillation with the frequency of the driving force. In the absence of friction, the amplitude of $M^q_p(t)$ grows linearly in time, therefore the solution $M^q_{pp}(t)$ consists of a linearly divergent oscillation (in the absence of driving force) plus quadratically divergent oscillation due to the quadratic divergence of the amplitude of the driven force. Quadratic divergence dominates over linear divergence and, therefore, the second order stability derivative $M^q_{pp}(t)$ grows as t^2, which is a well-known result for the second order stability matrices for systems with regular dynamics.[30]

In the presence of noise, $M^q_p(t)$ either diverges or decays as $\exp(\lambda t)$ depending on the sign of λ as discussed previously. Thus, $M^q_{pp}(t)$ consists of two oscillation terms, with the amplitude of the first, the free oscillation term, behaving as $\exp(\lambda t)$ and the amplitude of the second, the driving force term, depending on time as $\exp(2\lambda t)$. If $\lambda>0$, the driving force term will dominate and the divergence of $M^q_{pp}(t)$ will be $\exp(2\lambda t)$. However, if $\lambda<0$, which we are mostly interested in, the decay of $M^q_{pp}(t)$ goes as $\exp(-\lambda t)$.

The divergence of the remaining second order stability matrix elements $M^q_{qq}(t)$, $M^q_{qp}(t)$, $M^p_{qq}(t)$, $M^p_{qp}(t)$, and $M^p_{pp}(t)$ will be the same as $M^q_{pp}(t)$ since they are obtained from $M^q_{pp}(t)$ either by integration or from a similar type of equations. It is straightforward to extend the same analysis to the higher order stability derivatives. We thus conclude that an

nth order stability matrix element $M^{(n)}(t)$ behaves at long times as t^n for an isolated regular system, $\exp(n\lambda t)$ for a dissipative regular system with positive λ, and $\exp(-|\lambda|t)$ for a dissipative regular system with negative λ.

For the analysis in Sec. VII we would also need the behavior of stability matrix elements at the initial interval of time. From the physical point of view, the effect of noise from surrounding contributes to system's dynamics with time, therefore at the very first moments of time we may consider the dynamics of a system coupled to environment to be similar to that of an isolated system, which means the divergence of the nth stability matrix as t^n. However, as we have shown, at long times stability matrix elements decay or diverge exponentially. The divergence of $M^{(n)}(t)$ at all times can be thus taken as a product of its initial and its long-time behavior, giving

$$M^{(n)}(t) = \begin{cases} t^n e^{2n\lambda t}, & \lambda > 0, \\ t^n e^{-|\lambda| t}, & \lambda < 0. \end{cases} \tag{6.2}$$

VII. ANALYSIS OF SEMICLASSICAL CORRECTIONS

Given the dynamic behavior of stability matrices it is now interesting to see how the semiclassical correction terms in Eq. (1.2) decay when a system-bath coupling is introduced. The order of magnitude of the first classical term in Eq. (1.2) is governed by its largest divergent derivative, $|\partial\alpha(t)/\partial J| \sim M^{(1)}(t)(\partial\omega/\partial J)|\alpha_{\max}|$, the second is of the order of its highest divergent derivative $|\partial^3\alpha(t)/\partial J^3| \sim (\{M^{(1)}(t) \times(\partial\omega/\partial J)\}^3)|\alpha_{\max}|$, where $|\alpha_{\max}|$ is the largest spectral component in the Fourier decomposition of $\alpha(t)$ and higher order derivatives $\partial^n\omega/\partial J^n$ are neglected (in particular, for the Morse oscillator, $\partial^2\omega/\partial J^2$ is exactly zero). The second term becomes significant when it is of the same magnitude as the first term $\hbar M^{(1)}(t)|\alpha_{\max}|^2(\partial\omega/\partial J) \simeq \hbar^3 M^{(1)} \times(t)^3|\alpha_{\max}|^2(\partial\omega/\partial J)^3$. This equality becomes satisfied at time t^* at which $M^{(1)}(t^*) = 1/\hbar|\partial\omega/\partial J|$ and, using Eq. (6.2), we have

$$t^* e^{\lambda t^*} = \frac{1}{\hbar\left|\dfrac{\partial\omega}{\partial J}\right|}, \tag{7.1}$$

which is true for both positive and negative λ. In the absence of system-bath coupling $\lambda = 0$, we recovered the result for the nondissipative regular motion.[7] The crossover time t^* stands for the critical time when the classical term fails to describe further quantum dynamics and higher order semiclassical corrections are needed. One can see from Eq. (6.1) that positive λ reduces t^* while the negative λ increases t^*. Interestingly, there is a critical value of λ, at which t^* becomes infinitely large. This happens when $\max_t(t\exp(\lambda_c t)) = 1/\hbar|\partial\omega/\partial J|$, which gives

$$\lambda_c = -e\hbar\left|\frac{\partial\omega}{\partial J}\right|. \tag{7.2}$$

As $\lambda \to \lambda_c + 0$, the crossover time $t^* \to \infty$ and for all $\lambda < \lambda_c$, the classical term in series (1.2) dominates over the rest of the semiclassical terms at *all* times and the system thus becomes completely classical. One can also notice that condition (7.2) removes the quantum recursion effects caused by summation over discrete levels in Eq. (1.1). The period of quantum recursions is inversely proportional to the difference of phase frequencies of nearby levels, i.e., by $\Delta\omega \approx \hbar|\partial\omega/\partial J|$, which follows from Eq. (7.2) and is on the order of the signal decay time $1/\lambda_c$. Therefore the summation in Eq. (1.1) can be replaced with classical integration.

We can illustrate the obtained results numerically by direct calculation of semiclassical terms in Eq. (1.2). We calculate the classical and two correction terms up to the order of $\hbar^4$, for a single term $R_n(t)$ in Eq. (1.1), i.e., the microcanonical response function, of a Morse potential coupled bilinearly to the bath of harmonic oscillators described earlier. The quantum and semiclassical linear response functions of an isolated Morse oscillator were computed in Ref. 7. The Morse potential $D(1-\exp(-\sigma x))^2$ is considered due to the simple analytical form of its action-angle representation, however, at the same time, in the low-energy region its anharmonicity can be represented by a single cubic term to make a connection with the results in the present paper. The parameter of cubic anharmonicity in this case is $\varepsilon = 3\sigma/4$, the harmonic frequency is $\Omega_0 = \sqrt{2D\sigma^2/\mu}$, and $\hbar|\partial\omega/\partial J| = 2\chi_e\Omega_0 = \sigma^2/\mu$, where χ_e is the spectral anharmonicity and μ is the mass. To obtain potential (3.2) with a particle of unitary mass $\mu = 1$, one needs to rescale the parameters according to $\gamma'(t) = \gamma(t)/\Omega_0^2$, $t' = \Omega_0 t$, and $T' = kT/2D\sigma^2$. The expression (5.8) for the exponent of $M^{(1)}(t)$ thus becomes

$$\lambda = \frac{e^{-\Omega_0/\omega_c}}{2}\left(-\gamma_0 + C'\frac{9\Omega_0 kT}{32D}\right). \tag{7.3}$$

From here, the critical strength of friction γ_0, which corresponds to the border of stability ($\lambda = 0$) of $M^{(1)}(t)$, reads

$$\gamma_0^b = \Omega_0\frac{9C'}{32}\frac{kT}{D}, \tag{7.4}$$

and the critical friction strength that makes the quantum system completely classical ($\lambda = \lambda_c$) is obtained from Eqs. (7.2) and (7.3),

$$\gamma_0^c = \gamma_0^b + 4\chi_e\Omega_0 e^{1+(\Omega_0/\omega_c)}. \tag{7.5}$$

We compare the results of numerical simulations with these two parameters γ_0^b and γ_0^c in Fig. 6. The parameters of simulations are $D = 50$, $\mu = 100$, $\sigma = 1.4$, $\hbar = 1$, $J_0 = 1.5$, and the temperature was taken to be equal to the initial energy $kT = J_0\Omega_0$. Both resonant and nonresonant harmonic baths were considered with the cutoff frequencies $\omega_c = 2\Omega_0$ and $\omega_c = 0.1\Omega_0$, respectively. Figure 5 shows the nonresonant case; one can see that the semiclassical expression converges to the classical one as the coupling strength is increased. In Fig. 6 the results for the resonance case is shown. One can see that for $\gamma_0 < \gamma_0^b$ the first two semiclassical correction terms are unstable. The increase in coupling strength $\gamma_0 > \gamma_0^c$ leads to the convergence of the semiclassical result to the classical one on a longer time scale. The divergence of semiclassical results at long times is due to the limited number of the calculated semiclassical corrections. The inclusion of higher

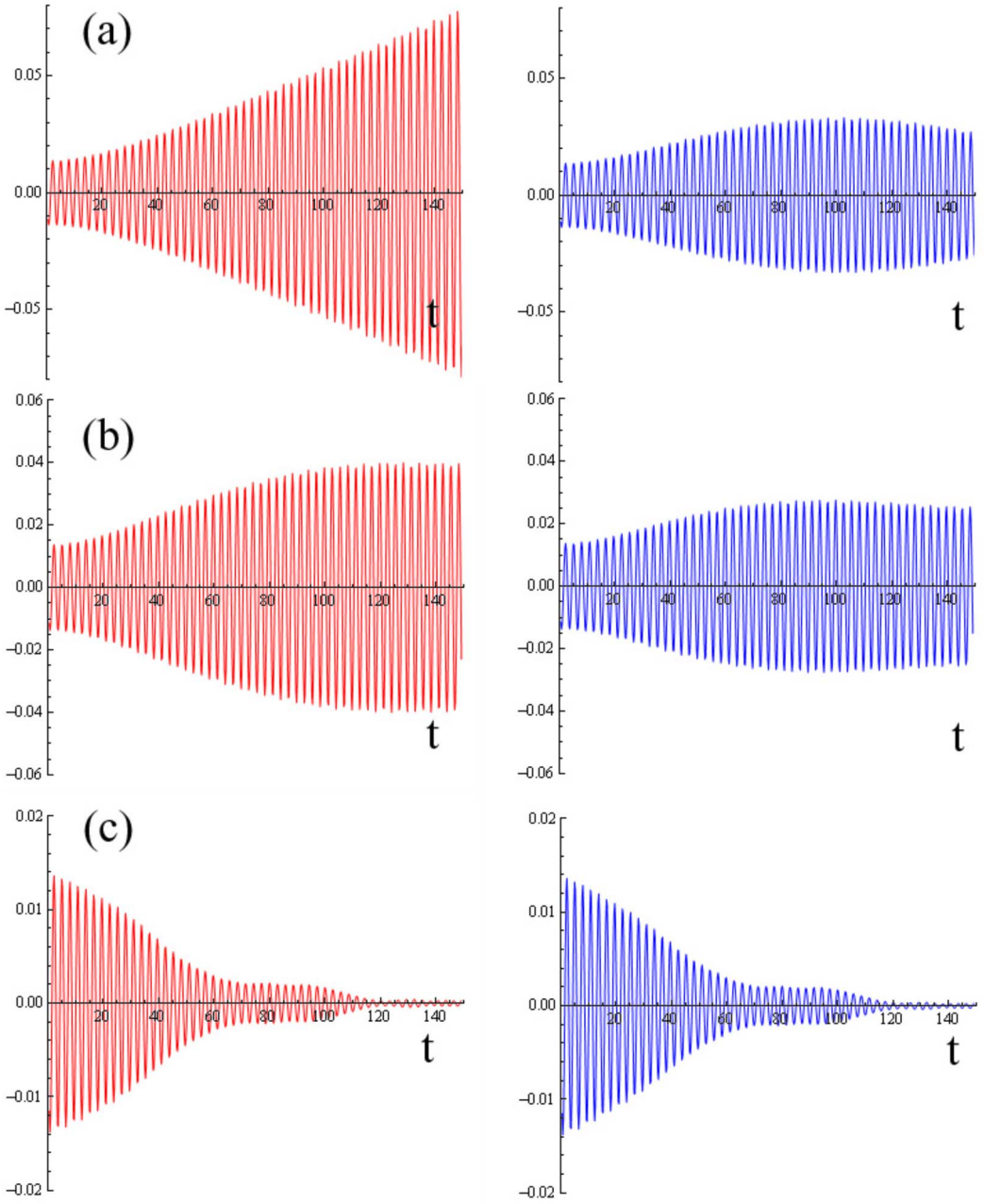

FIG. 5. (Color online) Linear response function calculated from Eq. (1.2) for the Morse oscillator coupled to a nonresonant bath with $\omega_c=0.1\omega_s$. The left column represents the classical result, while the right column represents the semiclassical result $O(\hbar^4)$. Plot (a) corresponds to an isolated system, plot (b) corresponds to the coupling strength $\gamma_0=0.03$, and plot (c) corresponds to the coupling strength $\gamma_0=0.5$.

order corrections is believed to converge the semiclassical result on longer time scale similar to the nondissipative case in Ref. 7. However, the main purpose of the present analysis is not to calculate the higher order corrections but instead to indicate when we do not need to calculate them.

VIII. DISCUSSIONS

In this paper we discuss the effects of dissipation on the behavior of semiclassical corrections for the systems with quasiperiodic dynamics. We have shown that the divergence of the corrections and thus their contributions to the overall semiclassical expression (1.2) can be significantly reduced by introducing the dissipation effects. One of the possible physical reasons for the reduction in divergence of stability matrices in the presence of dissipation is the increase in dimensionality of the system due to the additional degrees of freedom from the environment. It was shown[37,38] that additional degrees of freedom result in the decay of classical stability matrices if the dynamics of classical motion is chaotic. The classical response of chaotic systems is beyond the scope of our current analysis and its quantum-classical correspondence should be further explored.[39]

In the present analysis we studied the stability of matrix elements on the basis of stability of their equations of motion. In the nonresonant case, the process of pure dephasing leads to the blueshift of system's oscillation frequency and

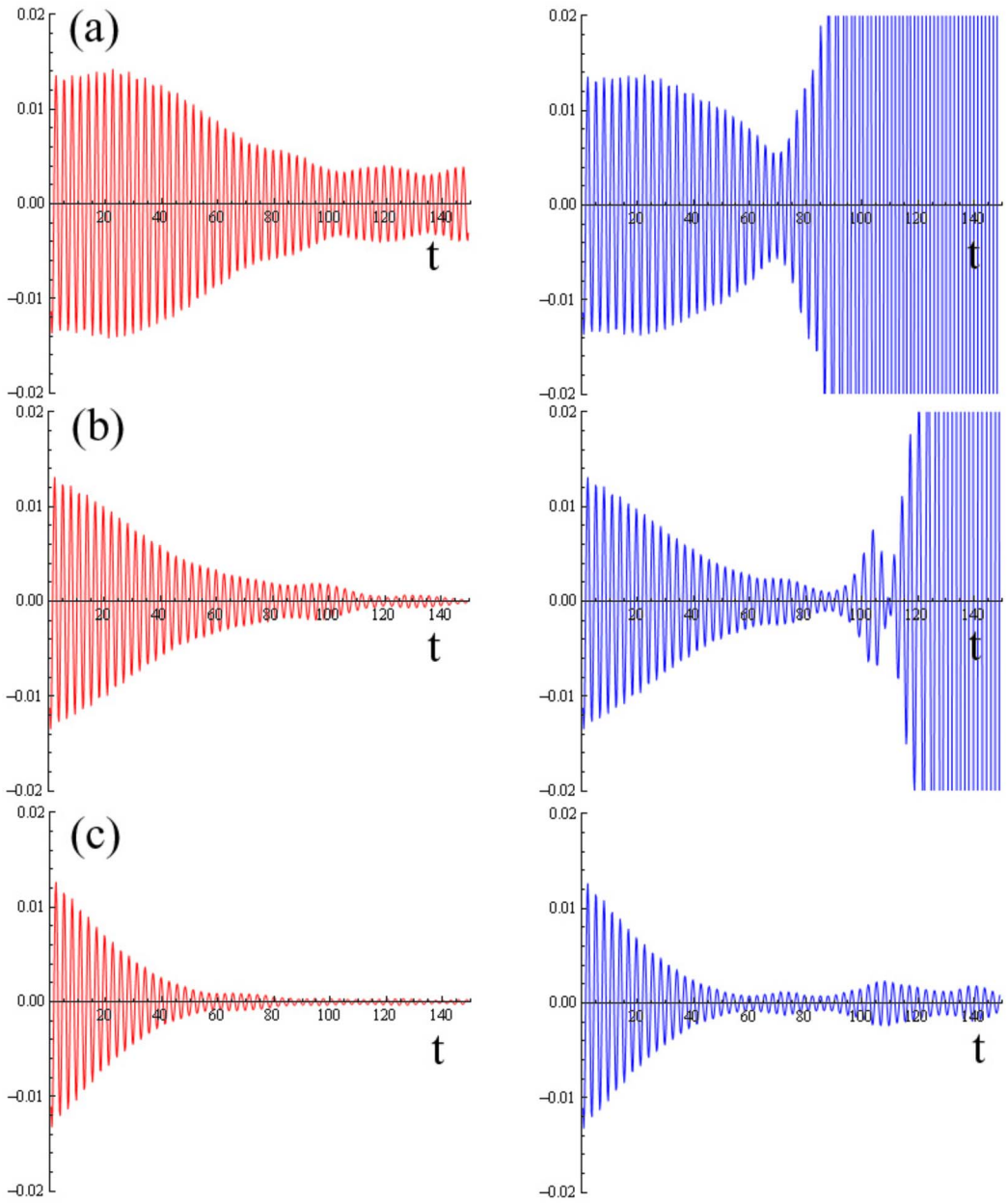

FIG. 6. (Color online) Linear response function calculated from Eq. (1.2) for the Morse oscillator coupled to a resonant bath with $\omega_c=2\omega_s$. The left column represents the classical result, while the right column represents the semiclassical result $O(\hbar^4)$. Plot (a) corresponds to the coupling strength $\gamma_0=0.01$, plot (b) corresponds to the coupling strength $\gamma_0=0.03$, and plot (c) corresponds to the coupling strength $\gamma_0=0.05$. The values of the critical coupling strengths are $\gamma_0^b=0.023$ and $\gamma_0^c=0.20$.

therefore to the decay of semiclassical corrections as well as the convergence of the semiclassical expression to its classical result. In the resonant case, when the spectrum of the bath contains modes with system's frequency, the semiclassical corrections can either diverge or converge depending on the value of coupling parameters. At values of bath friction and temperature, given by the criterion $\gamma_0 > \gamma_0^c$, the contribution of higher-order $\hbar^n$-terms to the semiclassical series (1.2) is much smaller than the contribution from the classical Poisson-bracket term and, therefore, at these and higher values of friction and temperature, the dynamics of system can be considered classically. The criterion $\gamma_0 > \gamma_0^c$ sets simple limits when the dynamics of quantum system can be described in terms of classical mechanics; one needs to compare the anharmonicity of a system with the parameters of bath and if they satisfy inequality $\gamma_0 > \gamma_0^c$, then the dynamics of the system is classical.

The method of semiclassical corrections in the form of stability derivatives is not a very efficient method from the computational point of view, since the numerical evaluation of higher order corrections requires precise calculation of divergent stability derivatives, the number of which grows exponentially with correction order. However, it provides an analytically simple and intuitive way of describing quantum-classical correspondence, exploring the effects of dissipation, and deriving an explicit criteria for the suppression of quantum effects.

Our extensive discussions on quantum-classical corre-

spondence in dissipative systems have important implications for condensed phase quantum dynamics simulations of pure liquids, solutions, solids, and polymer systems. The large number of degrees of freedom involved in these systems makes it necessary to calculate response functions with classical dynamics or approximate dynamic methods, including centroid molecular dynamics (CMD), ring polymer dynamics, Wigner dynamics, and various mixed quantum-classical methods.[40–44] However, it has been difficult to formulate a conceptual framework to understand the approximate nature of various trajectory-based methods. The key results of our analysis, the concept of crossover time, and its parametric dependence on the coupling strength to the dissipative environment provide a powerful tool in understanding and comparing approximate dynamic simulation approaches:

- Most MD simulations compute autocorrelation functions, but response functions are a natural choice for classical approximations. As explained in Ref. 7, the system's response to external perturbation is a physical process with direct analogy in classical mechanics and thus serves as a convenient starting point for our analysis. In contrast, quantum correlation functions are complex and cannot be directly accessed experimentally. For this reason, both CMD and ring polymer dynamics are designed to calculate response functions, i.e., the Kubo-transformed correlation function.[45,46]
- The definition of the crossover time confirms that classical and quantum response functions are identical for harmonic oscillators, thus suggesting a simple baseline for comparing various approximations. According to Eq. (7.1), classical dynamics is accurate at short times, but the deviation is expected after the crossover time, which is directly related to the deviation from harmonic potentials, i.e., anharmonicity.
- As expected, under strong friction, a quantum system loses phase coherence and assumes the characteristics of classical dynamics but with the quantum distribution function. Similar arguments can be applied to many-body systems, where the large number of degrees of freedom wash out quantum recurrence and leads to classical-like behavior. Thus, it is the regime of $\gamma > \gamma_c$ defined in Eq. (7.5) that centroid dynamics, ring polymer dynamics, and Winger dynamics can be reliably applied to condensed phase systems.

These conclusions, in particular, the dissipative effect, are consistent with earlier observations by several groups.[40–44] Our contribution lies in the rigorous formulation of a quantitative approach built on a systematic expansion of the exact quantum response function and the asymptotic analysis of the stability of dissipative trajectories, thus extending the principle of quantum-classical correspondence to a broad dynamic regime.

ACKNOWLEDGMENTS

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