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Nondivergent classical response functions from uncertainty principle: Quasiperiodic systems

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Time-divergence in linear and nonlinear classical response functions can be removed by taking a phase-space average within the quantized uncertainty volume O($\hbar^n$) around the microcanonical energy surface. For a quasiperiodic system, the replacement of the microcanonical distribution density in the classical response function with the quantized uniform distribution density results in agreement of quantum and classical expressions through Heisenberg's correspondence principle: each matrix element $\langle u|\alpha(t)|v\rangle$ corresponds to the $(u-v)$th Fourier component of $\alpha(t)$ evaluated along the classical trajectory with mean action $(J_u+J_v)/2$. Numerical calculations for one- and two-dimensional systems show good agreement between quantum and classical results. The generalization to the case of N degrees of freedom is made. Thus, phase-space averaging within the quantized uncertainty volume provides a useful way to establish the classical-quantum correspondence for the linear and nonlinear response functions of a quasiperiodic system.

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I. INTRODUCTION

Linear and nonlinear response functions carry complete microscopic information necessary for the calculation of optical measurements.[1,2] The difficulty of quantum mechanical calculations of the nonlinear response functions for large anharmonic systems provides a strong motivation for investigating the semiclassical approach for evaluating these observables.[3–6] The classical limit of the quantum response function is usually obtained by replacing commutation relations with Poisson brackets and neglecting terms in higher order of the Plank constant.[7] However, this leads to a vital difference between the results from quantum and classical approaches. The quantum response function is well-defined in terms of matrix elements and transition frequencies, whereas the simple classical limit of the response function diverges with time because of the instability of classical nonlinear dynamics.[8,9] For a given energy of the system, both linear and nonlinear classical response functions diverge. It was pointed out by van Kampen that even a weak perturbation leads to the failure of classical nonequilibrium perturbation theory at sufficiently long times.[10] Yet, while individual trajectories may be sensitive to the perturbation of initial conditions leading to the divergence of the classical linear response function, the phase space averaging over the initial density matrix eliminates these difficulties and makes linear response finite at all times.[3] Thus, averaging over the Boltzmann distribution successfully cancels the divergence and does not lead to practical difficulties in applying linear response theory. In fact, the ensemble averaged molecular dynamics simulation technique has been applied extensively in condensed phase vibrational spectroscopy. Similar problems arise for classical nonlinear response functions. Calculation of the latter involves evaluation of stability matrices, which diverge in time linearly for regular systems[8,11] and exponentially for chaotic systems.[9] It was thus noted that the stability matrix may be a sensitive probe of classical chaos.[3] Mukamel and Leegwater considered the question whether the thermal averaging over initial conditions can cancel the divergence of the nonlinear response function in the same way as it does for the linear response function.[8] They found that for a quartic oscillator the third-order response function $R^{(3)}(t_3=\text{const},0,t_1)$ indeed converges after thermal averaging. However, Noid, Ezra, and Loring have shown that $R^{(3)}(t,0,t)$ diverges even after thermal averaging for the canonical ensemble of noninteracting Morse oscillators.[5] Before this divergent behavior of the classical nonlinear response functions was pointed out, the molecular dynamics (MD) simulations of liquids supported the idea of convergence by Boltzmann averaging.[12–14] A many-body system in the thermodynamic limit such as liquid can be described with dissipative dynamics. Dissipation suppresses the interference among the classical trajectories making the nonlinear response function finite at all times. Nevertheless, for a nondissipative quasiperiodic dynamics, the thermal averaging over the initial density matrix does not necessarily remove divergence of the classical nonlinear response functions.[15] Thus, the problem of classical divergence is a conceptual question of quantum-classical correspondence, which is the subject of discussion of this paper.

An analytical approach to the calculation of the classical response function was reported in Ref. 6, where the algebraic structure of the one-dimensional Morse oscillator was explored. It was shown that the replacement of the microcanonical distribution function with the uniform distribution function of the width $\hbar$ and $2\hbar$ results in the exact quantum mechanical expression for the linear response function with linear polarization operator $\alpha=(b+b^+)$ and quadratic polarization operator $\alpha=(b+b^+)^2$, respectively, and almost ex-

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act expression for the second-order nonlinear response function with polarization operator $\alpha=(b+b^{+})^2$. Yet, a general form of polarization operator may result in divergence of the classical second and higher order response functions. In the present paper we generalize the approach proposed in Ref. 6 and show that using the uncertainty principle (or phase space quantization) we conveniently obtain the classical result that has well-defined quantum correspondence, both conceptually and numerically. We consider the quantum response function for a given eigenstate and its classical microcanonical limit. Starting with the classical expression for the response function we replace the microcanonical phase-space distribution density with the uniform distribution density within the phase-space volume $O(\hbar^n)$ around the classical trajectory. It may seem that this replacement should not lead to any considerable changes since in the classical limit $\hbar\to 0$ the latter distribution density becomes the microcanonical δ-function. Yet, the behavior of the classical response function changes drastically once the replacement is made. Finally we obtain the nondivergent classical expression which corresponds to the quantum mechanical one through Heisenberg's correspondence principle, where each time-dependent quantum matrix element $\langle u|\alpha(t)|v\rangle$ is replaced with the $(u-v)$th classical Fourier component of $\alpha(t)$, evaluated along the classical trajectory with mean action $(J_u+J_v)/2$.[11,16] This correspondence principle was also used in spectral analysis technique proposed in Ref. 17 and showed a good agreement between the quantum and semiclassical linear spectral intensities and frequencies. The semiclassical approach developed in the present paper has a convenient representation in action-angle variables. Thus we assume that the system under consideration with N degrees of freedom has N independent first integrals, i.e., the bounded motion in phase space is equivalent to motion on N torus.[18] This assumption restricts the variety of systems and includes only those with quasiperiodic motion, that is separable systems or nonseparable systems with a weak coupling.[7]

The paper is organized as follows: In Sec. II the expression for the linear response function of N-dimensional systems is obtained. We show in general that the uncertainty width $O(\hbar)$ is necessary to match classical and quantum results. In Sec. III the classical expression for the nonlinear response function is considered. Starting with the lowest order nonlinear response function we show that n-dimensional uncertainty $O(\hbar^n)$ around the microcanonical energy surface in multidimensional phase space is necessary to obtain a nondivergent classical formula for the nth-order nonlinear response function. Classical and quantum expressions for the nonlinear response function turn out to have the same form. The result is generalized for the system with N degrees of freedom. The numerical calculations for the second-order nonlinear response function of a two-dimensional system (coupled oscillators) are presented in Sec. IV, followed by general comments and conclusions in Sec. V.

II. LINEAR RESPONSE

The expression for the response function can be obtained by using time-dependent perturbation theory,[1,2] giving

$$R_Q^{(n)}(t_n,\ldots,t_0)=\left(\frac{i}{\hbar}\right)^n\langle[[\ldots[\alpha(t_n),\alpha(t_{n-1})],\ldots,\alpha(t_1)],\alpha(t_0)]\rangle, \tag{1}$$

where the operator $\alpha(t)$ stands for the time-dependent polarizability in Raman spectroscopy or the time-dependent dipole momentum in IR spectroscopy. The classical mechanical expression for the response function[3] may be obtained in the limit $\hbar\to 0$,

$$R_C^{(n)}(t_n,\ldots,t_0)=(-1)^n\langle\{\{\cdots\{\alpha(t_n),\alpha(t_{n-1})\},\ldots,\alpha(t_1)\},\alpha(t_0)\}\rangle, \tag{2}$$

where $\{\cdots\}$ are Poisson brackets. In this section we concentrate on the linear response function $R_Q^{(1)}(t)=(i/\hbar)\langle[\alpha(t),\alpha(0)]\rangle$ and its classical correspondence $R_C^{(1)}(t)=-\langle\{\alpha(t),\alpha(0)\}\rangle$. Using identity $\mathrm{Tr}[\{A,B\}C]=\mathrm{Tr}[A\{B,C\}]$ we write

$$R_C^{(1)}(t)=-\mathrm{Tr}(\{\alpha(t),\alpha(0)\}\rho)=-\mathrm{Tr}(\alpha(t)\{\alpha(0),\rho\}). \tag{3}$$

As mentioned in the introduction, we assume that the motion of the system is quasiperiodic, and therefore we consider classical response functions in action-angle variables, which can be found employing the technique of the EBK quantization.[19] Making use of the quasiperiodicity of motion in the limit of infinitely long time interval, $T\to\infty$, we can express any dynamical variable $f(t)$ as a convergent Fourier expansion:[7,11]

$$f(t)=\sum_{n_1n_2\ldots n_N}f_{n_1n_2\ldots n_N}e^{i(n_1\omega_1+n_2\omega_2+\cdots+n_N\omega_N)t} \tag{4}$$

or in terms of angle variables $\vec{\varphi}=\vec{\omega}t+\vec{\varphi}_0$ as

$$f(t)=\sum_{n_1n_2\cdots n_N}\tilde{f}_{n_1n_2\cdots n_N}e^{i(n_1\varphi_1+n_2\varphi_2+\cdots+n_N\varphi_N)}, \tag{5}$$

where $\{\omega_i\}$ are N fundamental frequencies and $\{\varphi_{0i}\}$ are N arbitrary constants. It is assumed that all frequencies ω_i are incommensurate. The fundamental frequencies are easy to obtain considering the Fourier transform of the generalized coordinates—the highest peak in the Fourier spectrum of such a coordinate corresponds to one fundamental frequency.[19] Action J_j can then be expressed in terms of fundamental frequencies and Fourier coefficients of Cartesian coordinates Q_j as[19]

$$J_j=\sum_{n_1n_2\ldots n_N}n_j(n_1\omega_1+n_2\omega_2+\cdots+n_N\omega_N)\times[|Q_{1n_1n_2\cdots n_N}|^2+|Q_{2n_1n_2\cdots n_N}|^2+\cdots+|Q_{Nn_1n_2\cdots n_N}|^2]. \tag{6}$$

The difficulty of practical application of the numerical EBK quantization grows with increasing the number of degrees of freedom N.[19] Yet, theoretically decomposition (5) may be applied to the system with arbitrary N, which allows analytical description of a many-body quasiperiodic systems. With this, we continue to consider classical response function in action-angle variables.

A. One-dimensional system

First, we consider a one-dimensional system with coordinates $\{J,\varphi\}$. The Poisson bracket in Eq. (3) is then

$$\{\alpha(0),\rho\}=\frac{\partial\alpha(0)}{\partial\varphi_0}\frac{\partial\rho}{\partial J}-\frac{\partial\alpha(0)}{\partial J}\frac{\partial\rho}{\partial\varphi_0}, \tag{7}$$

where ρ is the normalized distribution function. Considering distributions $\rho=\rho(J)$ uniform in φ, we will have only the first term in Eq. (7) and the classical expression for the linear response function in Eq. (3) is then

$$R_C^{(1)}(t)=-\oint d\varphi_0\, dJ\,\alpha(t)\frac{\partial\alpha(0)}{\partial\varphi_0}\frac{\partial\rho(J)}{\partial J}. \tag{8}$$

According to Eq. (5) we can express polarization $\alpha(t)$, a dynamical variable, as a Fourier series

$$\alpha(t)=\sum_n \alpha_n e^{in\varphi}, \tag{9}$$

where $\varphi=\omega t+\varphi_0$ and $\omega=d\varphi/dt=\partial E/\partial J$ is a fundamental frequency. On substituting Eq. (9) into Eq. (8) and integrating out φ_0 we have

$$R_C^{(1)}(t)=2\pi i\sum_n\int n|\alpha_n|^2 e^{in\omega t}\frac{\partial\rho(J)}{\partial J}dJ. \tag{10}$$

Considering microcanonical distribution $\rho=(1/2\pi)\delta(J-J_0)$, the integral in Eq. (10) gives well-known linear time divergence[10] of the classical response function

$$R_C^{(1)}(t)=\sum_n e^{in\omega t}\left(tn^2|\alpha_n|^2\frac{\partial\omega}{\partial J}-in\frac{\partial|\alpha_n|^2}{\partial J}\right)\Bigg|_{J=J_0}. \tag{11}$$

If, instead, we introduce an uncertainty Δ around the trajectory $J=J_0$,

$$\rho(J)=\begin{cases}\dfrac{1}{2\pi}\dfrac{1}{\Delta}, & J_0-\Delta/2<J<J_0+\Delta/2,\\ 0, & \text{otherwise,}\end{cases} \tag{12}$$

then Eq. (10) becomes

$$R_C^{(1)}(t)=\sum_n\frac{in}{\Delta}|\alpha_n|^2e^{in\omega t}|_{J=J_0-\Delta/2}-\sum_n\frac{in}{\Delta}|\alpha_n|^2e^{in\omega t}|_{J=J_0+\Delta/2}. \tag{13}$$

We now compare this result with quantum-mechanical formula for the linear response function

$$R_Q^{(1)}(t)=\sum_u\frac{i}{\hbar}|\langle g|\alpha|u\rangle|^2e^{-i(E_u-E_g)t/h}-\sum_u\frac{i}{\hbar}|\langle g|\alpha|u\rangle|^2e^{-i(E_g-E_u)t/h}, \tag{14}$$

and notice that they will have similar expressions if $\Delta=|n|\hbar$. This result was first observed in Ref. 6, where it was found that classical description of one-photon transition in the linear response of one-dimensional (1D) Morse oscillator will give exact results if $\Delta=\hbar$, and $\Delta=2\hbar$ for the two-photon transition. Indeed, let us show that the classical expression

$$R_C^{(1)}(t)=\sum_n\frac{i}{\hbar}|\alpha_n|^2e^{in\omega t}|_{J=J_0-n\hbar/2}-\sum_n\frac{i}{\hbar}|\alpha_n|^2e^{in\omega t}|_{J=J_0+n\hbar/2} \tag{15}$$

gives the exact result for the 1D Morse oscillator. We consider the simplest case of linear polarization operator $\alpha=b+b^+$ which has the following classical limit for the Morse oscillator:[6]

$$\alpha_c=\frac{2}{\chi_e\sqrt{1/\chi_e-1}}\left(\frac{\chi_e^2J^2}{\hbar^2}-\frac{\chi_eJ}{\hbar}\right)^{1/2}\cos(\varphi), \tag{16}$$

where $\varphi=[1-(2\chi_eJ/\hbar)]\omega_0t+\varphi_0$ and $\omega_0=\sqrt{2D\beta^2/\mu}$ with $\chi_e=\hbar\beta/\sqrt{8D\mu}$ are the parameters for the Morse potential. Polarization (16) has only two Fourier components, therefore

$$\begin{aligned}R_C^{(1)}(t)={}&-\frac{i}{\hbar}|\alpha_{-1}|^2e^{-i\omega t}|_{J=J_0-\hbar/2}+\frac{i}{\hbar}|\alpha_1|^2e^{i\omega t}|_{J=J_0-\hbar/2}\\&-\frac{i}{\hbar}|\alpha_{-1}|^2e^{-i\omega t}|_{J=J_0+\hbar/2}+\frac{i}{\hbar}|\alpha_1|^2e^{i\omega t}|_{J=J_0+\hbar/2}\\={}&\frac{2}{(1-\chi_e)\hbar}((v+1)(1-\chi_e(v+1))\\&\times\sin[(1-2\chi_e(v+1))\omega_0t]-v(1-\chi_ev)\\&\times\sin[(1-2\chi_ev)\omega_0t]),\end{aligned} \tag{17}$$

where the quantization condition $J_0=\hbar(v+1/2)$ was used. The last expression coincides with the quantum result.[6]

B. Two-dimensional system

Next, we examine the classical response function for the two-dimensional system (coupled oscillators). By analogy to Eq. (8) the expression for the classical response function is

$$\begin{aligned}R_C^{(1)}(t)={}&-\oint d\varphi_{0x}\,d\varphi_{0y}\,dJ_x\,dJ_y\,\alpha(t)\\&\times\left(\frac{\partial\alpha(0)}{\partial\varphi_{0x}}\frac{\partial\rho(J_x,J_y)}{\partial J_x}+\frac{\partial\alpha(0)}{\partial\varphi_{0y}}\frac{\partial\rho(J_x,J_y)}{\partial J_y}\right),\end{aligned} \tag{18}$$

where we again use the fact that distribution ρ is uniform in φ_{0x} and φ_{0y}. Fourier decomposition of polarization $\alpha(t)=\Sigma_{n_xn_y}\alpha_{n_xn_y}e^{i(n_x\varphi_x+n_y\varphi_y)}$ yields

$$\begin{aligned}R_C^{(1)}(t)={}&4\pi^2i\sum_{n_xn_y}\int dJ_x\,dJ_y|\alpha_{n_xn_y}|^2e^{i(n_x\omega_x+n_y\omega_y)t}\\&\times\left(n_x\frac{\partial}{\partial J_x}+n_y\frac{\partial}{\partial J_y}\right)\rho(J_x,J_y).\end{aligned} \tag{19}$$

Microcanonical distribution function $\rho(J_x,J_y) = (1/4\pi^2)\,\delta(J_x-J_{x0})\,\delta(J_y-J_{y0})$, which comes as a limit of quantum mechanical eigenstate, again results in the linear time divergence of the classical response function (19). Yet, as in the case of 1D system we may introduce uncertainty $O(\hbar)$ around the trajectory to remove this divergence. First, we notice that our two-dimensional $(2D)$ problem with the transition frequency $n_x\omega_x+n_y\omega_y$ can be converted into the 1D problem with one-photon transition on frequency $\tilde{\omega}_x$ after the change of variables,

$$\begin{aligned}
\tilde{J}_x &= \frac{n_x}{n_x^2+n_y^2}J_x + \frac{n_y}{n_x^2+n_y^2}J_y\,,\\
\tilde{J}_y &= \frac{n_y}{n_x^2+n_y^2}J_x - \frac{n_x}{n_x^2+n_y^2}J_y\,,\\
\tilde{\omega}_x &= \frac{\partial E}{\partial \tilde{J}_x} = \frac{\partial E}{\partial J_x}\frac{\partial J_x}{\partial \tilde{J}_x} + \frac{\partial E}{\partial J_y}\frac{\partial J_y}{\partial \tilde{J}_x} = \omega_x n_x + \omega_y n_y\,,\\
\tilde{\omega}_y &= \frac{\partial E}{\partial \tilde{J}_y} = \frac{\partial E}{\partial J_x}\frac{\partial J_x}{\partial \tilde{J}_y} + \frac{\partial E}{\partial J_y}\frac{\partial J_y}{\partial \tilde{J}_y} = \omega_x n_y - \omega_y n_x\,.
\end{aligned} \tag{20}$$

The classical response function now becomes

$$R_C^{(1)}(t) = 4\pi^2 i \sum_{n_x n_y} \int d\tilde{J}_x\, d\tilde{J}_y |\alpha_{n_x n_y}|^2 e^{i\tilde{\omega}_x t} \frac{\partial}{\partial \tilde{J}_x}\rho(\tilde{J}_x,\tilde{J}_y), \tag{21}$$

with the microcanonical density $\rho(\tilde{J}_x,\tilde{J}_y) = (1/4\pi^2)\,\delta(\tilde{J}_x - \tilde{J}_{x0})\,\delta(\tilde{J}_y-\tilde{J}_{y0})$. Integrating out $\tilde{J}_y$ we get

$$R_C^{(1)}(t) = i\sum_{n_x n_y}\left(\int d\tilde{J}_x |\alpha_{n_x n_y}|^2 e^{i\tilde{\omega}_x t}\frac{\partial}{\partial \tilde{J}_x}\delta(\tilde{J}_x-\tilde{J}_{x0})\right)\Bigg|_{\tilde{J}_y=\tilde{J}_{y0}}, \tag{22}$$

which is the same as the one-dimensional linear response function (10). As previously we now introduce uncertainty $\Delta=\hbar$, which changes microcanonical distribution density $\delta(\tilde{J}_x-\tilde{J}_{x0})$ to the uniform distribution density within the width $\hbar$, $(1/\hbar)\,\theta((\tilde{J}_x-\tilde{J}_{x0})+\hbar/2)\,\theta(\hbar/2-(\tilde{J}_x-\tilde{J}_{x0}))$. This results in

$$\begin{aligned}
R_C^{(1)}(t) = {} & \sum_{n_x n_y}\frac{i}{\hbar}|\alpha_{n_x n_y}|^2 e^{i\tilde{\omega}_x t}\Bigg|_{\substack{\tilde{J}_x=\tilde{J}_{x0}-\hbar/2\\ \tilde{J}_y=\tilde{J}_{y0}}}\\
& -\sum_{n_x n_y}\frac{i}{\hbar}|\alpha_{n_x n_y}|^2 e^{i\tilde{\omega}_x t}\Bigg|_{\substack{\tilde{J}_x=\tilde{J}_{x0}+\hbar/2\\ \tilde{J}_y=\tilde{J}_{y0}}},
\end{aligned} \tag{23}$$

or in terms of the old variables $\{J_x,J_y\}$ the classical expression for the linear response function becomes

$$\begin{aligned}
R_C^{(1)}(t) = {} & \sum_{n_x n_y}\frac{i}{\hbar}|\alpha_{n_x n_y}|^2 e^{i(n_x\omega_x+n_y\omega_y)t}\Bigg|_{\substack{J_x=J_{x0}-n_x\hbar/2\\ J_y=J_{y0}-n_y\hbar/2}}\\
& -\sum_{n_x n_y}\frac{i}{\hbar}|\alpha_{n_x n_y}|^2 e^{i(n_x\omega_x+n_y\omega_y)t}\Bigg|_{\substack{J_x=J_{x0}+n_x\hbar/2\\ J_y=J_{y0}+n_y\hbar/2}}.
\end{aligned} \tag{24}$$

From here it follows that in order to describe the transition on frequency $n_x\omega_x+n_y\omega_y$ in classical language, we need to run the classical trajectory that corresponds to the mean values of actions

$$\begin{aligned}
J_x = J_{x0}+n_x\hbar/2 &= \hbar(v_x+1/2)+n_x\hbar/2\\
&= (\hbar(v_x+1/2)+\hbar(v_x+n_x+1/2))/2\\
&= (J_{x0}+J_{xf})/2,\\
J_y = J_{y0}+n_y\hbar/2 &= \hbar(v_y+1/2)+n_y\hbar/2\\
&= (\hbar(v_y+1/2)+\hbar(v_y+n_y+1/2))/2\\
&= (J_{y0}+J_{yf})/2,
\end{aligned} \tag{25}$$

where J_{x0} and J_{y0} are action variables of the initial semiclassical state and J_{xf} and J_{yf} are action variables of the excited semiclassical state.

We now generalize the expression for the linear response function to the N-dimensional case (N degrees of freedom). Rotating and scaling N-dimensional action space similar to transformations (20) to get $\tilde{\omega}_1 = \partial E/\partial \tilde{J}_1 = \Sigma_i^N \omega_i n_i$ we reduce the N-dimensional problem to one-dimensional problem with effective action $\tilde{J}_1$ as in Eq. (22). Imposing the uncertainty $\hbar$ around $\tilde{J}_1$ and transforming action-space back, we obtain the general expression for the classical linear response function of the system with N degrees of freedom,

$$\begin{aligned}
R_C^{(1)}(t) = {} & \sum_{n_1 n_2 \ldots n_N}\frac{i}{\hbar}|\alpha_{n_1 n_2\ldots n_N}|^2 e^{i(\Sigma^N n_j\omega_j)\cdot t}\Bigg|_{\vec{J}=\vec{J}_0-\vec{n}\hbar/2}\\
& -\sum_{n_1 n_2 \ldots n_N}\frac{i}{\hbar}|\alpha_{n_1 n_2\cdots n_N}|^2 e^{i(\Sigma^N n_j\omega_j)\cdot t}\Bigg|_{\vec{J}=\vec{J}_0+\vec{n}\hbar/2},
\end{aligned} \tag{26}$$

which means that one should run classical trajectory with mean actions $J_j=(J_{j0}+J_{jf})/2$, $j=1,\ldots,N$, to find classical spectral amplitude $R_C^{(1)}(\omega)$ of the transition with frequency $\omega=\Sigma_j^N n_j\omega_j$.

The result in (26) reproduces the well-known Heisenberg's correspondence principle[11,16,17] between the quantum matrix element $\langle u|\alpha(t)|v\rangle$ and the classical $(u-v)$th Fourier component of $\alpha(t)$, evaluated along the trajectory with mean action $(J_u+J_v)/2$. This correspondence turns out to be almost exact for several exactly solvable systems such as harmonic and Morse oscillators[11] and explains the coincidence of classical and quantum results noted in Ref. 6 and in the preceding section.

III. NONLINEAR RESPONSE

The nonlinear response function contains more detailed dynamical information than the linear response function. First, we focus on the lowest order nonlinear response function,

$$R^{(2)}(\tau_1,\tau_2)=-\frac{1}{\hbar^2}\langle[[\alpha(t_2),\alpha(t_1)],\alpha(0)]\rangle, \tag{27}$$

where $t_2=\tau_1+\tau_2$, $t_1=\tau_1$. The Fourier–Laplace transform of the second-order response function is defined as

$$\tilde{R}^{(2)}(\tilde{\omega}_1,\tilde{\omega}_2)=\int_0^\infty d\tau_1\int_0^\infty d\tau_2\, R^{(2)}(\tau_1,\tau_2)\times\exp(i\tilde{\omega}_1\tau_1+i\tilde{\omega}_2\tau_2). \tag{28}$$

It is convenient to work with the symmetrized spectrum[2,20,21]

$$S(\Omega_1,\Omega_2)=|\tilde{R}^{(2)}(\Omega_1,\Omega_1+\Omega_2)+\tilde{R}^{(2)}(\Omega_2,\Omega_1+\Omega_2)|, \tag{29}$$

which contains all the information about 2D response in the range of $(\Omega_1>0,|\Omega_2|<\Omega_1)$.

In the Heisenberg representation the time dependence of the polarization operator is given by $\alpha(t)=e^{iH_0t/\hbar}\alpha(0)e^{-iH_0t/\hbar}$. The quantum expression for $R^{(2)}(\tau_1,\tau_2)$ can be written as

$$\begin{aligned}R_Q^{(2)}(\tau_1,\tau_2)&=-\frac{1}{\hbar^2}\langle g|[[\alpha(\tau_1+\tau_2),\alpha(\tau_1)],\alpha(0)]|g\rangle\\&=-\frac{1}{\hbar^2}\sum_v\sum_u\langle g|\alpha(0)|u\rangle\langle u|\alpha(0)|v\rangle\langle v|\alpha(0)|g\rangle[\exp(i(E_g-E_u)(\tau_1+\tau_2)/\hbar)\exp(i(E_u-E_v)\tau_1/\hbar)\\&\quad-\exp(i(E_u-E_v)(\tau_1+\tau_2)/\hbar)\exp(i(E_g-E_u)\tau_1/\hbar)-\exp(i(E_u-E_v)(\tau_1+\tau_2)/\hbar)\exp(i(E_v-E_g)\tau_1/\hbar)\\&\quad+\exp(i(E_v-E_g)(\tau_1+\tau_2)/\hbar)\exp(i(E_u-E_v)\tau_1/\hbar)],\end{aligned} \tag{30}$$

where E_k is an energy eigenvalue that corresponds to a specific eigenstate $|k\rangle\equiv|k_1,k_2,\ldots,k_N\rangle$ of the system with N degrees of freedom. State $|g\rangle$ is the initial state which is not necessarily the ground state. As mentioned previously, to obtain the classical limit for the response function we should change quantum commutators to Poisson brackets,

$$R_C^{(2)}(\tau_1,\tau_2)=\langle\{\{\alpha(t_2),\alpha(t_1)\},\alpha(0)\}\rangle. \tag{31}$$

Again, we use action-angle variables to describe classical motion. In the preceding section it was shown that the number of degrees of freedom does not play any important role, therefore we start our considerations with the one-dimensional system with coordinates $\{J,\varphi\}$. As shown in Appendix A the nonlinear response function (31) will have the following expression:

$$R_C^{(2)}(\tau_1,\tau_2)=\int dJ\int_0^{2\pi}d\varphi_0\left(\frac{\partial\alpha(t_2)}{\partial\varphi_0}\frac{\partial\alpha(t_1)}{\partial J}-\frac{\partial\alpha(t_2)}{\partial J}\frac{\partial\alpha(t_1)}{\partial\varphi_0}\right)\frac{\partial\alpha(0)}{\partial\varphi_0}\frac{\partial\rho}{\partial J}. \tag{32}$$

Now we make use of the quasiperiodicity of motion to decompose $\alpha(t)$ into fundamental frequencies as we did

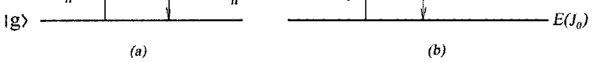

FIG. 1. The consecutive transitions from the quantum (a) and the classical single-trajectory (b) approaches. The simple classical method on the single trajectory gives only one average frequency $\omega_c=\omega(J_0+\Delta/2)$, which corresponds to action $J_0+\Delta/2$, and therefore is not able to account for $\Delta\omega(|g\rangle\rightarrow|u\rangle)\neq\Delta\omega(|u\rangle\rightarrow|v\rangle)$.

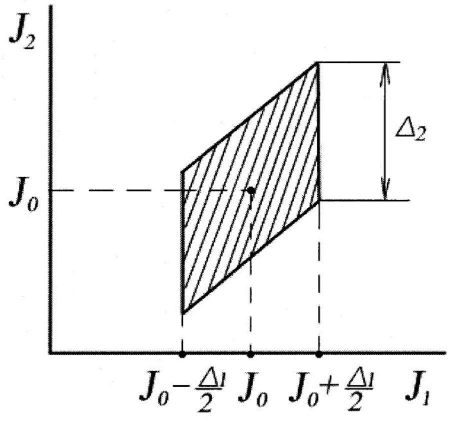

FIG. 2. Distribution density $\rho(J_1,J_2,J_3)$ for the second-order response function in the (J_1,J_2) plane.

in Eq. (9) for the linear response function $\alpha(t) = \Sigma_n \alpha_n e^{in(\omega t+\varphi_0)}$. Substituting it into Eq. (32) and integrating out φ_0 we get

$$R_C^{(2)}(\tau_1,\tau_2) = i\sum_n \sum_m \left\{ \int dJ(n+m)\left(m\alpha_m \frac{\partial \alpha_n}{\partial J} - n\alpha_n \frac{\partial \alpha_m}{\partial J}\right) \times \alpha_{-n-m}\frac{\partial \rho}{\partial J} e^{in\omega t_1 + im\omega t_2} + imn(m+n) \times (t_1-t_2)\int \alpha_m \alpha_n \alpha_{-n-m} \frac{\partial \omega}{\partial J}\frac{\partial \rho}{\partial J} e^{in\omega t_1 + im\omega t_2} dJ \right\}. \tag{33}$$

Microcanonical distribution density $\rho=(1/2\pi)\delta(J-J_0)$ again leads to the time divergence of the response function (33). If we now impose uncertainty $\Delta = \mathrm{O}(\hbar)$ with the distribution density given by Eq. (12) we will still have time divergence due to the second term in Eq. (33). Yet, if $mn=0$ there will be no second term and we may describe spectral peaks $(\Omega_1,\Omega_2)=\{(0,m\omega),(m\omega,0),(n\omega,-n\omega)\}$ of symmetrized spectrum $\mathrm{S}(\Omega_1,\Omega_2)$ with formula (33) using density (12); these are transitions that involve only two states. Thus, one can see that by considering single classical trajectory with uncertainty $\mathrm{O}(\hbar)$ around it one can correctly describe transitions between two states—the case of linear response function and the case of nonlinear response function for transitions $(\Omega_1,\Omega_2)=\{(0,m\omega),(m\omega,0),(n\omega,-n\omega)\}$. The latter explains the nondivergence of the second-order response function with quadratic polarization obtained in Ref. 6. Indeed, polarization $\alpha=(b+b^+)^2$ results only in spectral peaks $(\Omega_1,\Omega_2)=\{(0,2\omega),(2\omega,0),(2\omega,-2\omega)\}$, therefore phase averaging within uncertainty $2\hbar$ does not lead to the divergence of the classical response function at long times.

A. One-dimensional system

Yet, in general the second-order response function involves transitions between three states (Fig. 1). Therefore one trajectory is not sufficient. We need to employ multiple trajectories in our method. This will solve one more problem of the quantum-classical correspondence—the correct account of anharmonicity effects on the frequencies of transitions between successive states (Fig. 1). It was impossible to do so having only one fundamental frequency from the single trajectory simulation. The multiple trajectories concept is usually used to calculate stability matrices in the classical expression of the nonlinear response function.[3] Yet, stability matrices diverge. To overcome this difficulty we propose another approach. First, we start with introducing additional variables to the classical expression of the nonlinear response function (31) as shown in Appendix B:

$$R_C^{(2)}(\tau_1,\tau_2) = \int \{\{\alpha(J_3,\varphi_3),\alpha(J_2,\varphi_2)\}_3,\alpha(J_1,\varphi_0)\}_3 \times \frac{1}{2\pi}\delta(J_1-J_0)\,\delta(J_2-J_1) \times \delta(J_3-J_1)dJ_1\,dJ_2\,dJ_3\,d\varphi_0, \tag{34}$$

where $\varphi_3=\omega(J_3)t_2+\varphi_0$, $\varphi_2=\omega(J_2)t_1+\varphi_0$ and brackets $\{\cdots\}_3$ are defined as

$$\{A,B\}_3 = \frac{\partial A}{\partial \varphi_0}\left(\frac{\partial}{\partial J_1}+\frac{\partial}{\partial J_2}+\frac{\partial}{\partial J_3}\right)B - \frac{\partial B}{\partial \varphi_0} \times \left(\frac{\partial}{\partial J_1}+\frac{\partial}{\partial J_2}+\frac{\partial}{\partial J_3}\right)A. \tag{35}$$

Polarizations α in Eq. (34) are now evaluated on three separate trajectories, which at this step have the same initial conditions $J_1=J_2=J_3=J_0$, $\varphi_{20}=\varphi_{30}=\varphi_0$. We can also consider Eq. (34) in another way—as a trajectory in four-dimensional space $\{J_1,J_2,J_3,\varphi\}$ with microcanonical distribution density

$$\rho(J_1,J_2,J_3) = \frac{1}{2\pi}\delta(J_1-J_0)\,\delta(J_2-J_1)\,\delta(J_3-J_1). \tag{36}$$

As previously our main assumption is that this microcanonical distribution function $\rho(J_1,J_2,J_3)$ can be replaced with the uniform distribution function within volume $\mathrm{O}(\hbar^2)$ around the trajectory $\{(J_1,J_2,J_3,\varphi):J_1=J_2=J_3=J_0\}$. In Appendix C such an uncertainty volume is found from the condition of the *nondivergence* [i.e., absence of derivatives $\partial\alpha(t)/\partial J_j$] of the classical response function (34) (see Fig. 2), which is provided by the distribution density

$$\rho(J_1,J_2,J_3) = \frac{1}{2\pi\Delta_1\Delta_2}\theta((J_1-J_0)+\Delta_1/2)\,\theta((\Delta_1/2) -(J_1-J_0))\,\theta((J_2-J_1)+\Delta_2/2)\,\theta((\Delta_2/2) -(J_2-J_1))\,\delta\left(J_3+\frac{n}{m}J_2-\frac{n+m}{m}J_1\right). \tag{37}$$

With distribution (37) the classical expression for the second-order response function, as shown in Appendix C, becomes

$$
\begin{aligned}
R_C^{(2)}(\tau_1,\tau_2)=\sum_{n,m}\frac{-(m+n)m}{\Delta_1\Delta_2}\Bigg\{&\alpha_m(J_3)\alpha_n(J_2)\alpha_{-m-n}(J_1)\exp(im\omega(J_3)(\tau_1+\tau_2)+in\omega(J_2)\tau_1)\Bigg|_{\substack{J_1=J_0+\Delta_1/2\\ J_2=J_0+\Delta_2/2+\Delta_1/2\\ J_3=J_0+(\Delta_1-\Delta_2(n/m))/2}}\\
&-\alpha_m(J_3)\alpha_n(J_2)\alpha_{-m-n}(J_1)\exp(im\omega(J_3)(\tau_1+\tau_2)+in\omega(J_2)\tau_1)\Bigg|_{\substack{J_1=J_0-\Delta_1/2\\ J_2=J_0+\Delta_2/2-\Delta_1/2\\ J_3=J_0-(\Delta_1+\Delta_2(n/m))/2}}\\
&-\alpha_m(J_3)\alpha_n(J_2)\alpha_{-m-n}(J_1)\exp(im\omega(J_3)(\tau_1+\tau_2)+in\omega(J_2)\tau_1)\Bigg|_{\substack{J_1=J_0+\Delta_1/2\\ J_2=J_0-\Delta_2/2+\Delta_1/2\\ J_3=J_0+(\Delta_1+\Delta_2(n/m))/2}}\\
&+\alpha_m(J_3)\alpha_n(J_2)\alpha_{-m-n}(J_1)\exp(im\omega(J_3)(\tau_1+\tau_2)+in\omega(J_2)\tau_1)\Bigg|_{\substack{J_1=J_0-\Delta_1/2\\ J_2=J_0-\Delta_2/2-\Delta_1/2\\ J_3=J_0-(\Delta_1-\Delta_2(n/m))/2}}\Bigg\}. \qquad (38)
\end{aligned}
$$

Comparing classical result (38) with quantum result (30) we can see that the forms of the two expressions are the same. As in the case of the linear response function the arbitrariness of the size of the uncertainty volume for the classical nonlinear response function (Fig. 2) is removed from the requirement of coincidence of quantum and classical expressions, i.e., for $\Delta_1=|n+m|\hbar$ and $\Delta_2=|m|\hbar$. With this, the final formula for the classical second-order response function takes the following form:

$$
\begin{aligned}
R_C^{(2)}(\tau_1,\tau_2)=\sum_{n,m}\frac{-1}{\hbar^2}\Bigg\{&\alpha_m(J_3)\alpha_n(J_2)\alpha_{-m-n}(J_1)\exp(im\omega(J_3)(\tau_1+\tau_2)+in\omega(J_2)\tau_1)\Bigg|_{\substack{J_1=J_0+(n+m)\hbar/2\\ J_2=J_0+m\hbar+(n\hbar/2)\\ J_3=J_0+m\hbar/2}}\\
&-\alpha_m(J_3)\alpha_n(J_2)\alpha_{-m-n}(J_1)\exp(im\omega(J_3)(\tau_1+\tau_2)+in\omega(J_2)\tau_1)\Bigg|_{\substack{J_1=J_0-(n+m)\hbar/2\\ J_2=J_0-n\hbar/2\\ J_3=J_0-n\hbar-(m\hbar/2)}}\\
&-\alpha_m(J_3)\alpha_n(J_2)\alpha_{-m-n}(J_1)\exp(im\omega(J_3)(\tau_1+\tau_2)+in\omega(J_2)\tau_1)\Bigg|_{\substack{J_1=J_0+(n+m)\hbar/2\\ J_2=J_0+n\hbar/2\\ J_3=J_0+n\hbar+(m\hbar/2)}}\\
&+\alpha_m(J_3)\alpha_n(J_2)\alpha_{-m-n}(J_1)\exp(im\omega(J_3)(\tau_1+\tau_2)+in\omega(J_2)\tau_1)\Bigg|_{\substack{J_1=J_0-(n+m)\hbar/2\\ J_2=J_0-m\hbar-(n\hbar/2)\\ J_3=J_0-m\hbar/2}}\Bigg\}. \qquad (39)
\end{aligned}
$$

Careful comparison of quantum expression (30) and classical expression (39) shows that again each quantum-mechanical propagator $\langle v|\alpha|u\rangle\exp(i(E_v-E_u)t/\hbar)$ is replaced with the Fourier component $\alpha_{v-u}(J)\times\exp(i(v-u)\omega(J)t)|_{J=(J_v+J_u)/2}$ in the classical formula. Therefore, for instance, to calculate the classical second-order response of the 1D system in the process shown in Fig. 1(a), one should run three classical trajectories $\{J,\varphi_0\}$ with actions $J_0+n\hbar/2$, $J_0+n\hbar+m\hbar/2$, $J_0+(n+m)\hbar/2$ and find fundamental frequencies and spectral components of $\alpha(t)$ along these trajectories. One can check that formula (39) reproduces almost exact quantum result for the one-dimensional Morse oscillator with quadratic polarization[5] $\alpha=(b+b^+)^2$, as shown in Ref. 6.

B. *n*th-order response function for multidimensional systems

The result (39) can be generalized for the system with N degrees of freedom. As it was shown for the linear response function, by scaling and rotating multidimensional action space we may reduce a N-dimensional problem to a one dimensional one. As an example, the second part of Appendix B contains transformations for the second-order response function of two-dimensional systems. The final formula for the N-dimensional system have the same result as for one-dimensional system but with vectors instead of scalars [compare Eq. (15) with Eq. (26)]. The second-order classical response function for the N-dimensional system reads

$$\begin{aligned} R_C^{(2)}(\tau_1,\tau_2)=\sum_{n,m}\frac{-1}{\hbar^2}\Bigg\{ & \alpha_{\vec m}(\vec J_3)\,\alpha_{\vec n}(\vec J_2)\,\alpha_{-\vec m-\vec n}(\vec J_1)\exp(i\vec m\vec\omega(\vec J_3)(\tau_1+\tau_2)+i\vec n\vec\omega(\vec J_2)\tau_1)\Bigg|_{\substack{\vec J_1=\vec J_0+(\vec n+\vec m)\hbar/2\\ \vec J_2=\vec J_0+\vec m\hbar+(\vec n\hbar/2)\\ \vec J_3=\vec J_0+\vec m\hbar/2}} \\ & -\alpha_{\vec m}(\vec J_3)\,\alpha_{\vec n}(\vec J_2)\,\alpha_{-\vec m-\vec n}(\vec J_1)\exp(i\vec m\vec\omega(\vec J_3)(\tau_1+\tau_2)+i\vec n\vec\omega(\vec J_2)\tau_1)\Bigg|_{\substack{\vec J_1=\vec J_0-(\vec n+\vec m)\hbar/2\\ \vec J_2=\vec J_0-\vec n\hbar/2\\ \vec J_3=\vec J_0-\vec n\hbar-(\vec m\hbar/2)}} \\ & -\alpha_{\vec m}(\vec J_3)\,\alpha_{\vec n}(\vec J_2)\,\alpha_{-\vec m-\vec n}(\vec J_1)\exp(i\vec m\vec\omega(\vec J_3)(\tau_1+\tau_2)+i\vec n\vec\omega(\vec J_2)\tau_1)\Bigg|_{\substack{\vec J_1=\vec J_0+(\vec n+\vec m)\hbar/2\\ \vec J_2=\vec J_0+\vec n\hbar/2\\ \vec J_3=\vec J_0+\vec n\hbar+(\vec m\hbar/2)}} \\ & +\alpha_{\vec m}(\vec J_3)\,\alpha_{\vec n}(\vec J_2)\,\alpha_{-\vec m-\vec n}(\vec J_1)\exp(i\vec m\vec\omega(\vec J_3)(\tau_1+\tau_2)+i\vec n\vec\omega(\vec J_2)\tau_1)\Bigg|_{\substack{\vec J_1=\vec J_0-(\vec n+\vec m)\hbar/2\\ \vec J_2=\vec J_0-\vec m\hbar-(\vec n\hbar/2)\\ \vec J_3=\vec J_0-\vec m\hbar/2}}\Bigg\}, \end{aligned} \tag{40}$$

where $\vec J_k=(J_{k_1},J_{k_2},\ldots,J_{k_N})$, $\alpha_{\vec m}=\alpha_{m_1m_2\ldots m_N}$ and $\vec m\vec\omega=m_1\omega_1+m_2\omega_2+\cdots+m_N\omega_N$.

Basing on the results for the first- and second-order response functions it becomes possible to find the classical result for the *n*th order response function. As it was noticed previously the difference between the results for the N-dimensional system and for the one-dimensional system is that all scalar parameters of the 1D system turn to the N-component vectors. Therefore, for the purpose of simplicity, we may consider only one-dimensional systems. The classical expression (15) for the linear response function can be rewritten in the form

$$\begin{aligned} R_C^{(1)}(t)=&\sum_n\frac{i}{\hbar}\alpha_n(J_1)\,\alpha_{-n}(J_2)\,e^{in\omega(J_2)t}\Bigg|_{\substack{J_1=J_0-n\hbar/2\\ J_2=J_0-n\hbar/2}} \\ &-\sum_n\frac{i}{\hbar}\alpha_n(J_1)\,\alpha_{-n}(J_2)\,e^{in\omega(J_2)t}\Bigg|_{\substack{J_1=J_0+n\hbar/2\\ J_2=J_0+n\hbar/2}} \end{aligned} \tag{41}$$

with distribution density within the volume O($\hbar$) in three-dimensional space $\{J_1,J_2,\varphi_0\}$ given by

$$\rho(J_1,J_2)=\frac{1}{2\pi}\frac{1}{|n|\hbar}\tilde\theta_{|n|\hbar}(J_1-J_0)\,\delta(J_2-J_1), \tag{42}$$

where $\tilde\theta_\Delta(x)=\theta(x+\Delta/2)\,\theta(\Delta/2-x)$ is a square function of the width Δ. Comparing Eq. (42) with Eq. (37) it becomes clear, that in order to obtain the nondivergent classical expression for the *n*th-order nonlinear response function, one should impose uncertainty within the volume O($\hbar^n$) around the trajectory in $(n+1)$-dimensional phase space. The uncertainty volume is given for each sequence of transitions $|k_0\rangle\rightarrow|k_0+k_1\rangle\rightarrow|k_0+k_1+k_2\rangle\rightarrow\cdots\rightarrow|k_0+\cdots+k_n\rangle\rightarrow|k_0\rangle$ by the distribution density

$$\rho(J_1,J_2,\ldots,J_{n+1})=\frac{1}{2\pi}\,\frac{1}{|k_1|\hbar\times|k_1+k_2|\hbar\times|k_1+k_2+k_3|\hbar\times\cdots}\times\tilde{\theta}_{|k_1|\hbar}(J_1-J_0)\times\tilde{\theta}_{|k_1+k_2|\hbar}\left(J_2-\frac{k_1}{k_1}J_1\right)$$
$$\times\tilde{\theta}_{|k_1+k_2+k_3|\hbar}\left(J_3-\frac{k_2}{k_1+k_2}J_2-\frac{k_1}{k_1+k_2}J_1\right)\times\cdots\times\tilde{\theta}_{|k_1+\cdots+k_n|\hbar}\left(J_n-\frac{k_{n-1}}{k_1+k_2+\cdots+k_{n-1}}J_{n-1}\right.$$
$$\left.-\cdots-\frac{k_1}{k_1+k_2+\cdots+k_{n-1}}J_1\right)\delta\left(J_{n+1}-\frac{k_n}{k_1+k_2+\cdots+k_n}J_n-\cdots-\frac{k_1}{k_1+k_2+\cdots+k_n}J_1\right). \tag{43}$$

Again, distribution functions (43) result in the replacement of the quantum mechanical matrix elements $\langle v|\alpha|u\rangle$ with the Fourier coefficients of $\alpha(t)$, evaluated along the classical trajectory with average action $(J_v+J_u)/2$. The latter can be verified by the detailed calculation of the third-order response function $R_C^{(3)}(\tau_1,\tau_2,\tau_3)$ using the distribution density in Eq. (43). It is useful to check that in the limit $\hbar\rightarrow 0$ the distribution density (43) becomes a microcanonical density in the form of the product of δ-functions as in Eq. (36).

IV. NUMERICAL CALCULATIONS

In this section we show how one can numerically implement the above results. We compute the second-order nonlinear response function of the two coupled oscillators and compare its symmetrized spectra $S(\Omega_1,\Omega_2)$ from quantum and classical calculations. We consider Henon–Heiles Hamiltonian[22]

$$H=\tfrac{1}{2}(p_x^2+p_y^2+\omega_x^0x^2+\omega_y^0y^2)+\lambda(xy^2+\eta\cdot x^3) \tag{44}$$

with $\omega_x^0=0.7$, $\omega_y^0=1.3$, $\lambda=-0.1$, $\eta=0.1$.

The symmetrized spectrum of the second-order response function is given by Eq. (29). The Fourier–Laplace transform $\tilde{R}^{(2)}(\tilde{\omega}_1,\tilde{\omega}_2)$ of the quantum-mechanical result (30) is

$$\tilde{R}_Q^{(2)}(\tilde{\omega}_1,\tilde{\omega}_2)=-\frac{1}{4\hbar^2}\sum_v\sum_u\langle g|\alpha(0)|u\rangle\langle u|\alpha(0)|v\rangle\langle v|\alpha(0)|g\rangle[\delta(\tilde{\omega}_1-(E_g-E_v)/\hbar)\,\delta(\tilde{\omega}_2-(E_g-E_u)/\hbar)$$
$$-\delta(\tilde{\omega}_1-(E_g-E_v)/\hbar)\,\delta(\tilde{\omega}_2-(E_u-E_v)/\hbar)-\delta(\tilde{\omega}_1-(E_u-E_g)/\hbar)\,\delta(\tilde{\omega}_2-(E_u-E_v)/\hbar)$$
$$+\delta(\tilde{\omega}_1-(E_u-E_g)/\hbar)\,\delta(\tilde{\omega}_2-(E_v-E_g)/\hbar)]. \tag{45}$$

The Hamiltonian in Eq. (44) is diagonalized in a local mode basis of 225 harmonic oscillator wave functions and the quantum spectrum (45) of the second-order response function is calculated. We consider the polarization operator in the form

$$\alpha=x^2+y^2. \tag{46}$$

The symmetrized spectrum $S_Q(\Omega_1,\Omega_2)$ is plotted in Fig. 4(a). The system is considered to be initially in the state $|g\rangle=|1,1\rangle$.

The classical expression for $\tilde{R}^{(2)}(\tilde{\omega}_1,\tilde{\omega}_2)$ arises from the Fourier–Laplace transform of Eq. (40),

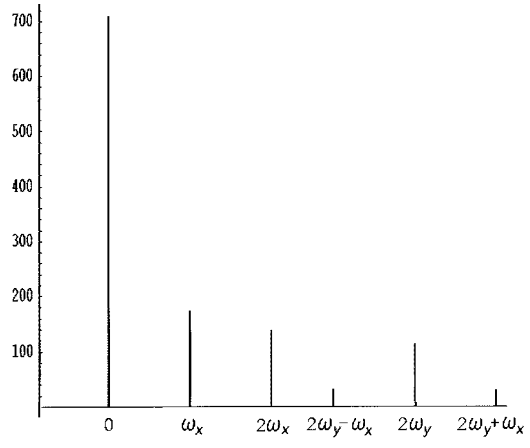

FIG. 3. Spectral components of $\alpha(t)=x^2+y^2$ in the region of the initial state $|1,1\rangle$. Representation of the spectral frequencies in terms of the fundamental frequencies $\{\omega_x,\omega_y\}$ leads to decomposition given by Eq. (5).

$$
\begin{aligned}
R_C^{(2)}(\tilde{\omega}_1,\tilde{\omega}_2)=\sum_{n_x,n_y,m_x,m_y}\frac{-1}{4\hbar^2}\Bigg\{ & \alpha_{m_xm_y}(\vec{J}_3)\,\alpha_{n_xn_y}(\vec{J}_2)\,\alpha_{-m_x-n_x,-m_y-n_y}(\vec{J}_1)\,\delta(\tilde{\omega}_1-\vec{m}\vec{\omega}(\vec{J}_3)-\vec{n}\vec{\omega}(\vec{J}_2)) \\
& \times\delta(\tilde{\omega}_2-\vec{m}\vec{\omega}(\vec{J}_3))\Bigg|_{\substack{\vec{J}_1=\vec{J}_0+(\vec{n}+\vec{m})\hbar/2\\ \vec{J}_2=\vec{J}_0+\vec{m}\hbar+(\vec{n}\hbar/2)\\ \vec{J}_3=\vec{J}_0+\vec{m}\hbar/2}} -\alpha_{m_xm_y}(\vec{J}_3)\,\alpha_{n_xn_y}(\vec{J}_2)\,\alpha_{-m_x-n_x,-m_y-n_y}(\vec{J}_1)\,\delta(\tilde{\omega}_1-\vec{m}\vec{\omega}(\vec{J}_3)-\vec{n}\vec{\omega}(\vec{J}_2)) \\
& \times\delta(\tilde{\omega}_2-\vec{m}\vec{\omega}(\vec{J}_3))\Bigg|_{\substack{\vec{J}_1=\vec{J}_0-(\vec{n}+\vec{m})\hbar/2\\ \vec{J}_2=\vec{J}_0-\vec{n}\hbar/2\\ \vec{J}_3=\vec{J}_0-\vec{n}\hbar-(\vec{m}\hbar/2)}} -\alpha_{m_xm_y}(\vec{J}_3)\,\alpha_{n_xn_y}(\vec{J}_2)\,\alpha_{-m_x-n_x,-m_y-n_y}(\vec{J}_1)\,\delta(\tilde{\omega}_1-\vec{m}\vec{\omega}(\vec{J}_3)-\vec{n}\vec{\omega}(\vec{J}_2)) \\
& \times\delta(\tilde{\omega}_2-\vec{m}\vec{\omega}(\vec{J}_3))\Bigg|_{\substack{\vec{J}_1=\vec{J}_0+(\vec{n}+\vec{m})\hbar/2\\ \vec{J}_2=\vec{J}_0+\vec{n}\hbar/2\\ \vec{J}_3=\vec{J}_0+\vec{n}\hbar+(\vec{m}\hbar/2)}} +\alpha_{m_xm_y}(\vec{J}_3)\,\alpha_{n_xn_y}(\vec{J}_2)\,\alpha_{-m_x-n_x,-m_y-n_y}(\vec{J}_1)\,\delta(\tilde{\omega}_1-\vec{m}\vec{\omega}(\vec{J}_3)-\vec{n}\vec{\omega}(\vec{J}_2)) \\
& \times\delta(\tilde{\omega}_2-\vec{m}\vec{\omega}(\vec{J}_3))\Bigg|_{\substack{\vec{J}_1=\vec{J}_0-(\vec{n}+\vec{m})\hbar/2\\ \vec{J}_2=\vec{J}_0-\vec{m}\hbar-(\vec{n}\hbar/2)\\ \vec{J}_3=\vec{J}_0-\vec{m}\hbar/2}}\Bigg\},
\end{aligned}
\tag{47}
$$

where $\vec{J}=(J_x,J_y)$, $\vec{\omega}=(\omega_x,\omega_y)$, $\vec{m}=(m_x,m_y)$, $\vec{n}=(n_x,n_y)$. Given the spectrum of $\alpha(t)$ one can select nonvanishing terms in the above sum. The typical Fourier spectrum of α in the vicinity of the initial state $|1,1\rangle$ is shown in Fig. 3. It has 11 significant spectral components: $\alpha_{0,0}$, $\alpha_{1,0}$, $\alpha_{2,0}$, $\alpha_{-1,2}$, $\alpha_{0,2}$, $\alpha_{1,2}$, $\alpha_{-1,0}$, $\alpha_{-2,0}$, $\alpha_{1,-2}$, $\alpha_{0,-2}$, $\alpha_{-1,-2}$, for which $\alpha_{-n_x,-n_y}=(\alpha_{n_x,n_y})^*$. Therefore the classical expression (47) will have only those values of $\vec{m}=(m_x,m_y)$, $\vec{n}=(n_x,n_y)$, which satisfy the equality

$$
\begin{aligned}
&\vec{m}+\vec{n}=\vec{k},\\
&\vec{m},\vec{n},\vec{k}\in\{(0,0),(1,0),(2,0),(-1,2),(0,2),(1,2),(-1,0),\\
&\qquad(-2,0),(1,-2),(0,-2),(-1,-2)\}.
\end{aligned}
\tag{48}
$$

In total, there will be 73 such combinations. To calculate the contributions of all the terms in the expression (47) we need to run 17 classical trajectories with action variables $J_x=\hbar(N_x+1/2)$, $J_y=\hbar(N_y+1/2)$, where the mean quantum numbers (N_x,N_y) are

$$
\begin{aligned}
&(0,1),\quad(0.5,1),\quad(1,1),\quad(1.5,1),\quad(2,1),\quad(2.5,1),\\
&(0,2),\quad(0.5,2),\quad(1,2),\quad(1.5,2),\quad(2,2),\quad(2.5,2),\\
&(0,3),\quad(0.5,3),\quad(1,3),\quad(1.5,3),\quad(2,3).
\end{aligned}
\tag{49}
$$

The above 17 trajectories are sufficient for calculating the complete two-dimensional classical spectrum for the system (44) with polarization (46). To run the above trajectories we need to find proper initial conditions, which will result in quantum numbers (49) according to formula (6). It was shown in Ref. 22 that the semiclassical spectrum of Henon–Heiles system reasonably agrees with the quantum mechanical one if the initial conditions were chosen by selecting J_i from the unperturbed Hamiltonian. Thus, we take mean quantum numbers (49) for unperturbed actions J_x, J_y and run classical trajectories keeping track of coordinates $x(t)$, $y(t)$ as well as $\alpha(x,y)$. Applying the Fourier transform to $x(t)$, $y(t)$, and $\alpha(t)$ evaluated on the same trajectory we select fundamental frequencies $\{\omega_x,\omega_y\}$ from the spectrum of $x(\omega_x,\omega_y)$, $y(\omega_x,\omega_y)$,[19] and find spectral components of α that correspond to these fundamental frequencies (e.g., Fig. 3). The results of classical simulations and corresponding quantum mechanical results are presented in Table I. The final symmetrized spectrum $S_C(\Omega_1,\Omega_2)$ from the classical calculations is shown in Fig. 4(b). Both Table I and Fig. 4 show good agreement of quantum and classical results. The discrepancy between quantum mechanical and classical calculations may arise from the following three reasons: (a) the semiclassical quantization does not result in the exact quantum mechanical spectrum, (b) the mean-action trajectory does not appropriately approximate the quantum matrix element, (c) the classical initial conditions do not lead to the desired quantized actions (6). The main error of the present calculations results from the fact, that in classical simulations we have used initial conditions of the unperturbed Hamiltonian. The latter can be improved by selecting better initial conditions.

V. CONCLUSIONS AND DISCUSSIONS

In the present paper we have found that the replacement of the microcanonical distribution density with the uniform

TABLE I. Quantum matrix elements and corresponding classical Fourier components for the two-dimensional Henon–Heiles system.

$\langle u_x u_y \vert \alpha(0) \vert v_x v_y \rangle$[a]	$\vert\langle u_x u_y \vert \alpha(0) \vert v_x v_y \rangle\vert$[a]	$\omega_Q = \vert E_u - E_v \vert/\hbar$[b]	$\alpha_{nx,ny}(N_x, N_y)$[c]	$\vert\alpha_{nx,ny}(N_x, N_y)\vert$[c]	$\omega_C = \vert n_x \omega_x + n_y \omega_y \vert$[d]
$\langle 0,1 \vert \alpha \vert 0,1 \rangle$	2.00	0	$\alpha_{0,0}(0,1)$	2.08	0
$\langle 0,0 \vert \alpha \vert 0,2 \rangle$	0.54	2.552	$\alpha_{0,2}(0,1)$	0.62	2.558
$\langle 0,1 \vert \alpha \vert 0,3 \rangle$	0.93	2.526	$\alpha_{0,2}(0,2)$	1.03	2.527
$\langle 0,2 \vert \alpha \vert 0,2 \rangle$	2.94	0	$\alpha_{0,0}(0,2)$	3.12	0
$\langle 0,3 \vert \alpha \vert 0,3 \rangle$	3.98	0	$\alpha_{0,0}(0,3)$	4.32	0
$\langle 0,2 \vert \alpha \vert 0,4 \rangle$	1.32	2.498	$\alpha_{0,2}(0,3)$	1.36	2.497
$\langle 0,0 \vert \alpha \vert 1,2 \rangle$	0.100	3.221	$\alpha_{1,2}(0.5,1)$	0.102	3.225
$\langle 0,1 \vert \alpha \vert 1,1 \rangle$	0.62	0.680	$\alpha_{1,0}(0.5,1)$	0.59	0.679
$\langle 0,2 \vert \alpha \vert 1,0 \rangle$	0.12	1.861	$\alpha_{1,2}(0.5,1)$	0.12	1.868
$\langle 0,1 \vert \alpha \vert 1,3 \rangle$	0.18	3.182	$\alpha_{1,2}(0.5,2)$	0.16	3.175
$\langle 0,2 \vert \alpha \vert 1,2 \rangle$	0.98	0.668	$\alpha_{1,0}(0.5,2)$	0.79	0.663
$\langle 1,1 \vert \alpha \vert 0,3 \rangle$	0.22	1.846	$\alpha_{1,2}(0.5,2)$	0.23	1.848
$\langle 0,3 \vert \alpha \vert 1,3 \rangle$	1.36	0.655	$\alpha_{1,0}(0.5,3)$	1.38	0.652
$\langle 0,2 \vert \alpha \vert 1,4 \rangle$	0.27	3.140	$\alpha_{1,2}(0.5,3)$	0.22	3.137
$\langle 0,4 \vert \alpha \vert 1,2 \rangle$	0.32	1.830	$\alpha_{1,2}(0.5,3)$	0.31	1.833
$\langle 1,1 \vert \alpha \vert 1,1 \rangle$	3.55	0	$\alpha_{0,0}(1,1)$	3.60	0
$\langle 0,1 \vert \alpha \vert 2,1 \rangle$	1.03	1.357	$\alpha_{2,0}(1,1)$	0.82	1.354
$\langle 1,1 \vert \alpha \vert 1,3 \rangle$	0.88	2.501	$\alpha_{0,2}(1,2)$	0.91	2.504
$\langle 1,2 \vert \alpha \vert 1,2 \rangle$	4.59	0	$\alpha_{0,0}(1,2)$	4.65	0
$\langle 0,2 \vert \alpha \vert 2,2 \rangle$	1.04	1.332	$\alpha_{2,0}(1,2)$	0.98	1.327
$\langle 1,3 \vert \alpha \vert 1,3 \rangle$	5.72	0	$\alpha_{0,0}(1,3)$	5.87	0
$\langle 1,2 \vert \alpha \vert 1,4 \rangle$	1.24	2.472	$\alpha_{0,2}(1,3)$	0.94	2.474
$\langle 0,3 \vert \alpha \vert 2,3 \rangle$	1.06	1.306	$\alpha_{2,0}(1,3)$	0.96	1.300
$\langle 1,1 \vert \alpha \vert 2,1 \rangle$	1.08	0.676	$\alpha_{1,0}(1.5,1)$	0.89	0.675
$\langle 1,1 \vert \alpha \vert 2,3 \rangle$	0.25	3.152	$\alpha_{1,2}(1.5,2)$	0.24	3.154
$\langle 2,1 \vert \alpha \vert 1,3 \rangle$	0.30	1.825	$\alpha_{-1,2}(1.5,2)$	0.21	1.830
$\langle 1,2 \vert \alpha \vert 2,2 \rangle$	1.61	0.664	$\alpha_{1,0}(1.5,2)$	1.25	0.662
$\langle 1,3 \vert \alpha \vert 2,3 \rangle$	2.18	0.650	$\alpha_{1,0}(1.5,3)$	2.12	0.648
$\langle 1,2 \vert \alpha \vert 2,4 \rangle$	0.38	3.107	$\alpha_{1,2}(1.5,3)$	0.32	3.106
$\langle 2,2 \vert \alpha \vert 1,4 \rangle$	0.43	1.808	$\alpha_{1,2}(1.5,3)$	0.46	1.810
$\langle 1,1 \vert \alpha \vert 3,1 \rangle$	1.78	1.349	$\alpha_{2,0}(2,1)$	1.65	1.346
$\langle 2,1 \vert \alpha \vert 2,1 \rangle$	5.15	0	$\alpha_{0,0}(2,1)$	5.18	0
$\langle 2,2 \vert \alpha \vert 2,2 \rangle$	6.27	0	$\alpha_{0,0}(2,2)$	6.30	0
$\langle 1,3 \vert \alpha \vert 3,3 \rangle$	1.83	1.295	$\alpha_{2,0}(2,3)$	1.47	1.292
$\langle 2,3 \vert \alpha \vert 2,3 \rangle$	7.52	0	$\alpha_{0,0}(2,3)$	7.61	0
$\langle 2,2 \vert \alpha \vert 2,4 \rangle$	1.16	2.443	$\alpha_{0,2}(2,3)$	1.03	2.447
$\langle 2,1 \vert \alpha \vert 3,1 \rangle$	1.59	0.672	$\alpha_{1,0}(2.5,1)$	1.24	0.669
$\langle 2,2 \vert \alpha \vert 3,2 \rangle$	2.26	0.659	$\alpha_{1,0}(2.5,2)$	2.06	0.658
$\langle 2,1 \vert \alpha \vert 3,3 \rangle$	0.31	3.120	$\alpha_{1,2}(2.5,2)$	0.30	3.123
$\langle 3,1 \vert \alpha \vert 2,3 \rangle$	0.35	1.803	$\alpha_{1,2}(2.5,2)$	0.34	1.808

[a] Matrix elements of the polarization operator in the eigenbasis of (44).

[b] Frequencies of transition between quantum states in the first column.

[c] Fourier components of $\alpha(t)$ calculated along the classical trajectories $J_x = \hbar(N_x + 1/2)$, $J_y = \hbar(N_y + 1/2)$ [each quantum mechanical matrix element $\langle v_x, v_y | \alpha | v_x + n_x, v_y + n_y \rangle$ corresponds to Fourier coefficient $\alpha_{n_n n_y}$ evaluated on the classical trajectory $J_x = \hbar(v_x + (n_x/2) + 1/2)$, $J_y = \hbar(v_y + (n_y/2) + 1/2)$].

[d] Frequencies of the Fourier components in the fourth column, $\tilde{\omega}_{n_x n_y} = n_x \omega_x(N_x, N_y) + n_y \omega_y(N_x, N_y)$.

density within volume $O(\hbar^n)$ in the expanded multidimensional phase space removes the inherent time divergence of the classical linear and nonlinear response functions. Each set of transitions, which corresponds to one term in quantum mechanical formula, defines a particular quantized phase-space uncertainty volume in the classical formula. The form of uncertainty volume is determined by the requirement of nondivergence of classical response function, which restricts the class of distribution functions and their arguments, and the requirement of a discrete spectrum, which selects only theta and delta functions in the expression for distribution density. The resulting classical response function is of the same form as the quantum response function for a given initial eigenstate. Classical and quantum expressions have well-defined one-to-one correspondence if the coefficients of the terms in the classical series are the same as those in the quantum formula. Setting these coefficients to be equal, we define the size of uncertainty volume and, in particular, justify the proposed phase-space quantization condition found empirically in Ref. 6. As a result, we arrive at Heisenberg's correspondence principle, where each matrix element $\langle u | \alpha(t) | v \rangle$ in the quantum formula corresponds to the classical Fourier $(u-v)$th coefficient of α(t). The same correspondence principle was used in the spectral analysis technique proposed in Ref. 17 and showed good numerical agreement between classical and quantum results. At the same time, for the nonlinear response, we arrive at the multiple trajectories approach, which avoids the divergent interference of classical trajectories.

One may speculate on the possible reasons for the construction of the uncertainty principle in classical response theory. We present a simple physical explanation below. The

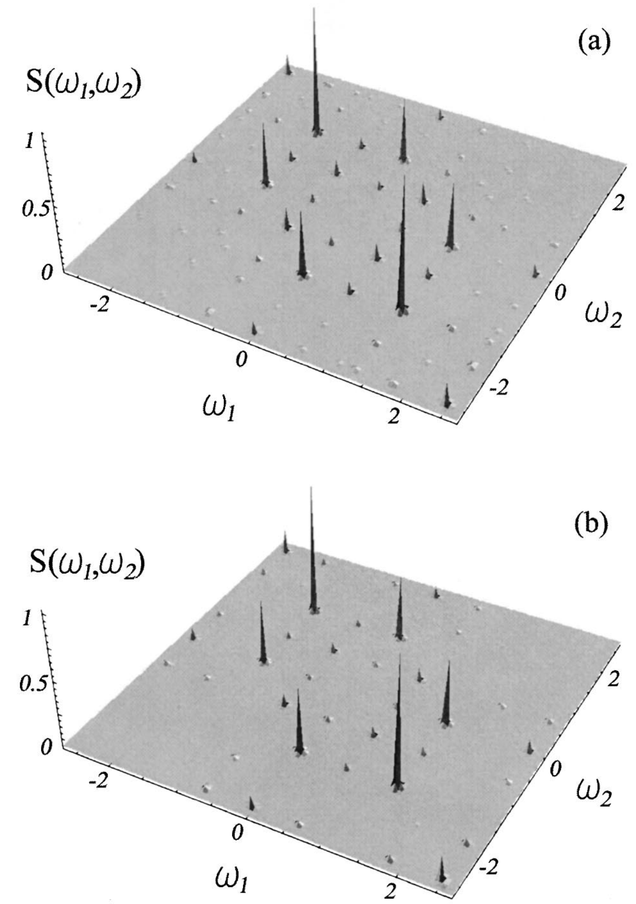

FIG. 4. Symmetrized 2D spectrum $S(\omega_1,\omega_2)$. (a) Quantum mechanical result [using formula (45)]; (b) classical result [using formula (47)].

energy of an isolated quantum mechanical system will not increase, i.e., a system will not respond to the external influence, unless a quantum transition occurs. And if it occurs, the action J, as pointed out by Bohr, changes discontinuously by $\Delta J = n\hbar$ for allowed n-photon transition. Our primary goal is to describe quantum mechanical response with classical dynamics. Yet, in classical mechanics there is no discontinuity—the influence of any force will result in an immediate continuous response of the system, therefore the smallest response of a classical system is zero. How is it possible to describe quantum dynamics, in which the smallest response of the system is $\Delta J = n\hbar$, with continuous theory (classical dynamics), in which the smallest response of the system is $\Delta J = 0$? One possible solution is to introduce the *uncertainty* $n\hbar$ to the latter. This is exactly what we have obtained in the present paper—to describe a n-photon transition in the response function we need to introduce the uncertainty $n\hbar$ for the classical action. Multiple independent transitions (in the case of nonlinear response) need multiple independent uncertainties, which results in uncertainty volume in the *expanded* action space. Therefore the expanded action space introduced in our approach is not just a result of algebraic manipulations, but is also based on intuitive physical argument. The latter also turns out to be in agreement with the results mentioned in the Introduction. Indeed, since the nonlinear response function needs a phase space averaging in the expanded phase space then the Boltzmann averaging, which is intrinsically an averaging within the original phase space, fails to converge the classical nonlinear response function for the constant-energy system with quasiperiodic motion. The concept of configurational or thermal averaging has been invoked in several classical and quasiclassical approximations of quantum dynamics, including wave-packet dynamics, nonadiabatic dynamics and centroid dynamics.[23–29] In the current context, phase space quantization can be generally established for quasiperiodic systems and leads to exact quantum mechanical results for a class of integrable Hamiltonians.

The results of this paper raise a conceptual question of whether the classical expression for the response function (2) is an appropriate limit of the quantum expression (1). Indeed, the theory of semiclassical quantization of the Poisson brackets[30,31] establishes the relation between quantum commutator and Poisson brackets in the form $[\hat{f},\hat{g}] = i\hbar\widehat{\{f,g\}} + \mathrm{O}(\hbar^2)$, where the remainders $\mathrm{O}(\hbar^2)$ are power series in $\hbar$ whose coefficients are bidifferential operators acting on f and g. The quantization parameter $\hbar$ is considered to be small but finite, thus $\mathrm{O}(\hbar^2)$ can be neglected as long as the prefactor of $\hbar^2$ is finite. However, this is not the case in response theory. The expression for quantum response function contains commutators $[\alpha(t_2),\alpha(t_1)]$ of the same dynamical operator $\alpha(t)$ taken at different times. Thus the differential operators in $\mathrm{O}(\hbar^2)$ will result in classical divergent derivatives $\partial^n x_k(t_2)/\partial x_j(t_1)^n$ (nth order stability matrices), which become infinitely large at times $t_2 \to \infty$ and elimination of these terms is not justified. We usually do not face the above problem since most applications of classical mechanics contain Poisson brackets of the functions evaluated at the same moment of time (for example, commutator of the dynamical function with Hamiltonian) and therefore we can always take instantaneous coordinates and momenta as system variables avoiding stability matrices. The $\mathrm{O}(\hbar^2)$ is thus finite and can be omitted in the limit of $\hbar \to 0$, resulting in the correspondence principle $[\hat{f},\hat{g}] \to i\hbar\{f,g\}$. Yet, we cannot do the same for the response function and the correct account of the higher order terms in $\hbar$ is also impossible. In the present paper we show that the classical response function can still be calculated as a limit of a quantum expression from the correspondence principle $[\hat{f},\hat{g}] \to i\hbar\{f,g\}$ if we change microcanonical δ-functions to square-functions of the width $\mathrm{O}(\hbar)$, $(1/n\hbar)\,\theta((J-J_0)+n\hbar/2)\,\theta(n\hbar/2-(J-J_0))$. Surprisingly as it may seem, while the replacement of the distribution functions lies within the error of $\mathrm{O}(\hbar)$, which is introduced as a result of eliminating higher order terms in the Plank constant, the classical response function changes drastically and becomes very close to quantum result once phase space is quantized.

The elucidation of the classical-quantum correspondence of response functions has both conceptual and practical implications: (1) Spectroscopic measurements are often interpreted in terms of classical dynamics. For example, an effective Hamiltonian has been used to describe the bending spectrum of acetene at high excitation energy from high-resolution spectroscopy.[32,33] Through classical or semiclassical approximations, the measured spectrum can then be mapped to normal-mode or local-mode motions solved from the effective Hamiltonian. Heisenberg's correspondence relation and its generalization to nonlinear response functions provide the theoretical basis for such mapping. (2) The dynamics of polyatomic molecules has stimulated topics such as intramolecular vibrational relaxation, isomerization, and energy localization.[34–43] A fundamental question is the manifestation of classical chaos in quantum dynamics and possible spectroscopic signals.[1,43–45] To address this question, we need to extend our formalism for quasiperiodic systems to a larger class of dynamic systems. (3) Of particular interest is the solute–solvent system, where the solvent must be treated classically and solute quantum mechanically.[24–28] The treatment usually leads to the inconsistency of mixed quantum-classical dynamics. Since the phase-space averaging introduces quantum dynamics through the initial conditions, we can in principle treat the solute and solvent on the same footing and thus avoid the difficulty of inconsistency. Yet, the implementation of this idea remains a challenge. (4) Another important direction to explore is the possibility of developing classical pictures of quantum concepts, such as phase coherence and relaxation. These pictures will advance our theoretical understanding of quantum coherence control[46–51] and vibrational line shapes.[52–58]

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APPENDIX A: SIMPLIFICATION OF CLASSICAL RESPONSE FUNCTIONS

In this Appendix we simplify the expression for the classical response function

$$\begin{aligned}R_C^{(2)}(\tau_1,\tau_2)&=\langle\{\{\alpha(t_2),\alpha(t_1)\},\alpha(0)\}\rangle\\&=\mathrm{Tr}(\{\{\alpha(t_2),\alpha(t_1)\},\alpha(0)\}\rho).\end{aligned}\tag{A1}$$

Using identity $\mathrm{Tr}[\{A,B\}C]=\mathrm{Tr}[A\{B,C\}]$ we find

$$\begin{aligned}&R_C^{(2)}(\tau_1,\tau_2)\\&\quad=\mathrm{Tr}(\{\alpha(t_2),\alpha(t_1)\},\{\alpha(0),\rho\})\\&\quad=\int dJ\int_0^{2\pi}d\varphi_0\left(\frac{\partial\alpha(t_2)}{\partial\varphi_0}\frac{\partial\alpha(t_1)}{\partial J}-\frac{\partial\alpha(t_2)}{\partial J}\frac{\partial\alpha(t_1)}{\partial\varphi_0}\right)\\&\qquad\times\left(\frac{\partial\alpha(0)}{\partial\varphi_0}\frac{\partial\rho}{\partial J}-\frac{\partial\alpha(0)}{\partial J}\frac{\partial\rho}{\partial\varphi_0}\right).\end{aligned}\tag{A2}$$

If ρ does not depend on φ, then

$$\begin{aligned}&R_C^{(2)}(\tau_1,\tau_2)\\&\quad=\mathrm{Tr}(\{\alpha(t_2),\alpha(t_1)\},\{\alpha(0),\rho\})\\&\quad=\int dJ\int_0^{2\pi}d\varphi_0\left(\frac{\partial\alpha(t_2)}{\partial\varphi_0}\frac{\partial\alpha(t_1)}{\partial J}-\frac{\partial\alpha(t_2)}{\partial J}\frac{\partial\alpha(t_1)}{\partial\varphi_0}\right)\\&\qquad\times\frac{\partial\alpha(0)}{\partial\varphi_0}\frac{\partial\rho}{\partial J}.\end{aligned}\tag{A3}$$

Another approach used in the text is

$$\begin{aligned}&R_C^{(2)}(\tau_1,\tau_2)\\&\quad=\mathrm{Tr}(\{\alpha(t_2),\alpha(t_1)\},\{\alpha(0),\rho\})\\&\quad=\mathrm{Tr}(\alpha(t_2),\{\alpha(t_1),\{\alpha(0),\rho\}\})\\&\quad=\int dJ\int_0^{2\pi}d\varphi_0\,\alpha(t_2)\left(\frac{\partial\alpha(t_1)}{\partial\varphi_0}\frac{\partial}{\partial J}\left(\frac{\partial\alpha(0)}{\partial\varphi_0}\frac{\partial\rho}{\partial J}\right)\right.\\&\qquad\left.-\frac{\partial\alpha(t_1)}{\partial J}\frac{\partial}{\partial\varphi_0}\left(\frac{\partial\alpha(0)}{\partial\varphi_0}\frac{\partial\rho}{\partial J}\right)\right)\end{aligned}\tag{A4}$$

which is obtained by successive applications of identity $\mathrm{Tr}[\{A,B\}C]=\mathrm{Tr}[A\{B,C\}]$.

APPENDIX B: EXPANDED PHASE SPACE

1. One-dimensional system

In this Appendix we introduce additional variables into the expression for the classical second-order response function and thus effectively increase the dimensionality of phase space. Using identity $\alpha(J_1)=\int\alpha(J_2)\,\delta(J_2-J_1)dJ_2$ we introduce variables J_2 and J_3 into the expression (31),

$$\begin{aligned}R_C^{(2)}(\tau_1,\tau_2)&=\int\{\{\alpha(J_1,\varphi_0,t_2),\alpha(J_1,\varphi_0,t_1)\},\alpha(J_1,\varphi_0,0)\}\frac{1}{2\pi}\delta(J_1-J_0)dJ_1\,d\varphi_0\\&=\int\left\{\left(\frac{\partial(\int\alpha_3(J_3)\,\delta(J_3-J_1)dJ_3)}{\partial\varphi_0}\frac{\partial(\int\alpha_2(J_2)\,\delta(J_2-J_1)dJ_2)}{\partial J_1}\right.\right.\\&\qquad\left.\left.-\frac{\partial(\int\alpha_3(J_3)\,\delta(J_3-J_1)dJ_3)}{\partial J_1}\frac{\partial(\int\alpha_2(J_2)\,\delta(J_2-J_1)dJ_2)}{\partial\varphi_0}\right),\alpha_1(J_1)\right\}\frac{1}{2\pi}\delta(J_1-J_0)dJ_1\,d\varphi_0\\&=\int\left\{\left(\frac{\partial\alpha_3(J_3)}{\partial\varphi_0}\delta(J_3-J_1)\cdot\alpha_2(J_2)\frac{\partial\delta(J_2-J_1)}{\partial J_1}-\alpha_3(J_3)\frac{\partial\delta(J_3-J_1)}{\partial J_1}\frac{\partial\alpha_2(J_2)}{\partial\varphi_0}\delta(J_2-J_1)\right),\alpha_1(J_1)\right\}\\&\qquad\times\frac{1}{2\pi}\delta(J_1-J_0)dJ_1\,dJ_2\,dJ_3\,d\varphi_0.\end{aligned}\tag{B1}$$

Using $\partial\delta(J_2-J_1)/\partial J_1=-\partial\delta(J_2-J_1)/\partial J_2$ and integrating by parts over J_3 and J_2 the terms in Eq. (B1), we obtain

$$\begin{aligned}R_C^{(2)}(\tau_1,\tau_2)&\\ &=\int\left\{\frac{\partial}{\partial\varphi_0}\left(\frac{\partial\alpha_3(J_3)}{\partial\varphi_0}\,\frac{\partial\alpha_2(J_2)}{\partial J_2}-\frac{\partial\alpha_3(J_3)}{\partial J_3}\,\frac{\partial\alpha_2(J_2)}{\partial\varphi_0}\right)\right.\\ &\quad\times\frac{\partial\alpha_1(J_1)}{\partial J_1}-\left[\left(\frac{\partial}{\partial J_2}+\frac{\partial}{\partial J_3}\right)\left(\frac{\partial\alpha_3(J_3)}{\partial\varphi_0}\,\frac{\partial\alpha_2(J_2)}{\partial J_2}\right.\right.\\ &\quad\left.\left.\left.-\frac{\partial\alpha_3(J_3)}{\partial J_3}\,\frac{\partial\alpha_2(J_2)}{\partial\varphi_0}\right)\right]\frac{\partial\alpha_1(J_1)}{\partial\varphi_0}\right\}\frac{1}{2\pi}\,\delta(J_1-J_0)\\ &\quad\times\delta(J_2-J_1)\,\delta(J_3-J_1)\,dJ_1\,dJ_2\,dJ_3\,d\varphi_0 \end{aligned}\tag{B2}$$

which is equivalent to

$$\begin{aligned}R_C^{(2)}(\tau_1,\tau_2)&\\ &=\int\{\{\alpha_3(J_3),\alpha_2(J_2)\}_3,\alpha_1(J_1)\}_3\,\frac{1}{2\pi}\,\delta(J_1-J_0)\\ &\quad\times\delta(J_2-J_1)\,\delta(J_3-J_1)\,dJ_1\,dJ_2\,dJ_3\,d\varphi_0,\end{aligned}\tag{B3}$$

where

$$\begin{aligned}\{A,B\}_3=&\frac{\partial A}{\partial\varphi_0}\left(\frac{\partial}{\partial J_1}+\frac{\partial}{\partial J_2}+\frac{\partial}{\partial J_3}\right)B\\ &-\frac{\partial B}{\partial\varphi_0}\left(\frac{\partial}{\partial J_1}+\frac{\partial}{\partial J_2}+\frac{\partial}{\partial J_3}\right)A.\end{aligned}$$

2. Two-dimensional system (two degrees of freedom)

Repeating the same steps (B1)–(B2) for the system with two degrees of freedom $\{J_x,J_y,\varphi_x,\varphi_y\}$ we will get the same expression as (B2) but with vectors $\vec{J}=(J_x,J_y)$ and $\vec{\varphi}_0=(\varphi_{0x},\varphi_{0y})$ instead of scalars J and φ_0. Substituting Fourier decomposition of α

$$\begin{aligned}\alpha_j(\vec{J}_j,\vec{\varphi}_j)&=\sum_{n_xn_y}\alpha_{n_xn_y}^{(j)}e^{(i(n_x\omega_x^{(j)}+n_y\omega_y^{(j)})\cdot t+i(n_x\varphi_{0x}+n_y\varphi_{0y}))}\\ &\equiv\sum_{\vec{n}}\tilde{\alpha}_{\vec{n}}^{(j)},\end{aligned}\tag{B4}$$

the classical second-order response function for the system with two degrees of freedom takes the form

$$\begin{aligned}R_C^{(2)}(\tau_1,\tau_2)=\sum_{\vec{n}_1\vec{n}_2\vec{n}_3}\int&\left\{i\left(i\tilde{\alpha}_{\vec{n}_3}^{(3)}\left[n_{3x}\frac{\partial}{\partial J_{2x}}+n_{3y}\frac{\partial}{\partial J_{2y}}\right]\tilde{\alpha}_{\vec{n}_2}^{(2)}-i\tilde{\alpha}_{\vec{n}_2}^{(2)}\left[n_{2x}\frac{\partial}{\partial J_{3x}}+n_{2y}\frac{\partial}{\partial J_{3y}}\right]\tilde{\alpha}_{\vec{n}_3}^{(3)}\right)\left[(n_{3x}+n_{2x})\frac{\partial}{\partial J_{1x}}+(n_{3y}+n_{2y})\frac{\partial}{\partial J_{1y}}\right]\right.\\ &\times\tilde{\alpha}_{\vec{n}_1}^{(1)}-i\tilde{\alpha}_{\vec{n}_1}^{(1)}\left[(n_{3x}+n_{2x})\left(\frac{\partial}{\partial J_{2x}}+\frac{\partial}{\partial J_{3x}}\right)+(n_{3y}+n_{2y})\left(\frac{\partial}{\partial J_{2y}}+\frac{\partial}{\partial J_{3y}}\right)\right]\left(i\tilde{\alpha}_{\vec{n}_3}^{(3)}\left[n_{3x}\frac{\partial}{\partial J_{2x}}+n_{3y}\frac{\partial}{\partial J_{2y}}\right]\right.\\ &\left.\left.\times\tilde{\alpha}_{\vec{n}_2}^{(2)}-i\tilde{\alpha}_{\vec{n}_2}^{(2)}\left[n_{2x}\frac{\partial}{\partial J_{3x}}+n_{2y}\frac{\partial}{\partial J_{3y}}\right]\tilde{\alpha}_{\vec{n}_3}^{(3)}\right)\right\}\frac{1}{4\pi^2}\,\delta(\vec{J}_1-\vec{J}_0)\,\delta(\vec{J}_2-\vec{J}_1)\,\delta(\vec{J}_3-\vec{J}_1)\,d\vec{J}_1\,d\vec{J}_2\,d\vec{J}_3\,d\vec{\varphi}_0,\end{aligned}\tag{B5}$$

where we have used the condition $\vec{n}_1+\vec{n}_2+\vec{n}_3=0$ for nonvanishing value of the integral over φ_0. Now we make transformations in six-dimensional space $\{J_{1x},J_{1y},J_{2x},J_{2y},J_{3x},J_{3y}\}$ and introduce new variables $\vec{\tilde{J}}_j=\vec{f}_j(\vec{J}_1,\vec{J}_2,\vec{J}_3)$, $j=1, 2, 3$. For the particular case of $n_{3x}n_{2y}\neq n_{2x}n_{3y}$ we take such variables $\vec{\tilde{J}}_j$ that

$$\frac{\partial}{\partial\tilde{J}_{1x}}=(n_{3x}+n_{2x})\frac{\partial}{\partial J_{1x}}+(n_{3y}+n_{2y})\frac{\partial}{\partial J_{1y}},$$

$$\frac{\partial}{\partial\tilde{J}_{2x}}=n_{3x}\left(\frac{\partial}{\partial J_{2x}}+\frac{\partial}{\partial J_{3x}}\right)+n_{3y}\left(\frac{\partial}{\partial J_{2y}}+\frac{\partial}{\partial J_{3y}}\right),\tag{B6}$$

$$\frac{\partial}{\partial\tilde{J}_{3x}}=n_{2x}\left(\frac{\partial}{\partial J_{2x}}+\frac{\partial}{\partial J_{3x}}\right)+n_{2y}\left(\frac{\partial}{\partial J_{2y}}+\frac{\partial}{\partial J_{3y}}\right).$$

With this, expression (B5) becomes

$$\begin{aligned}R_C^{(2)}(\tau_1,\tau_2)=\sum_{\vec{n}_1\vec{n}_2\vec{n}_3}\int&\left\{i\left(i\tilde{\alpha}_{\vec{n}_3}^{(3)}\frac{\partial}{\partial\tilde{J}_{2x}}\tilde{\alpha}_{\vec{n}_2}^{(2)}-i\tilde{\alpha}_{\vec{n}_2}^{(2)}\frac{\partial}{\partial\tilde{J}_{3x}}\tilde{\alpha}_{\vec{n}_3}^{(3)}\right)\frac{\partial}{\partial\tilde{J}_{1x}}\tilde{\alpha}_{\vec{n}_1}^{(1)}-i\tilde{\alpha}_{\vec{n}_1}^{(1)}\left(\frac{\partial}{\partial\tilde{J}_{2x}}+\frac{\partial}{\partial\tilde{J}_{3x}}\right)\left(i\tilde{\alpha}_{\vec{n}_3}^{(3)}\frac{\partial}{\partial\tilde{J}_{2x}}\tilde{\alpha}_{\vec{n}_2}^{(2)}-i\tilde{\alpha}_{\vec{n}_2}^{(2)}\frac{\partial}{\partial\tilde{J}_{3x}}\tilde{\alpha}_{\vec{n}_3}^{(3)}\right)\right\}\\ &\times\frac{1}{4\pi^2}\,\delta(\vec{J}_1(\vec{\tilde{J}}_1)-\vec{J}_0)\,\delta(\vec{J}_2(\vec{\tilde{J}}_2,\vec{\tilde{J}}_3)-\vec{J}_1(\vec{\tilde{J}}_1))\,\delta(\vec{J}_3(\vec{\tilde{J}}_2,\vec{\tilde{J}}_3)-\vec{J}_1(\vec{\tilde{J}}_1))\left|\frac{\partial\vec{J}}{\partial\vec{\tilde{J}}}\right|d\vec{\tilde{J}}_1\,d\vec{\tilde{J}}_2\,d\vec{\tilde{J}}_3\,d\vec{\varphi}_0\end{aligned}\tag{B7}$$

which after integrating out $\tilde{J}_{1y}$, $\tilde{J}_{2y}$, $\tilde{J}_{3y}$ has the same form as the one-dimensional expression (B2). The cases $n_{3x}n_{2y}=n_{2x}n_{3y}$ can be considered separately as well. Thus, each set of transitions $|g_1,g_2,\ldots,g_N\rangle\rightarrow|u_1,u_2,\ldots,u_N\rangle\rightarrow|v_1,v_2,\ldots,v_N\rangle\rightarrow|g_1,g_2,\ldots,g_N\rangle$ can be described by the appropriate series of transitions in the one-dimensional system $|\tilde{g}_1\rangle\rightarrow|\tilde{u}_1\rangle\rightarrow|\tilde{v}_1\rangle\rightarrow|\tilde{g}_1\rangle$.

APPENDIX C: UNCERTAINTY DISTRIBUTION DENSITY FOR TWO-TIME RESPONSE

In this Appendix we derive an explicit expression for the distribution density $\rho(J_1,J_2,J_3)$ that does not lead to the divergence of the classical expression for the second-order nonlinear response function

$$R_C^{(2)}(\tau_1,\tau_2)=\int\{\{\alpha(J_3,\varphi_3),\alpha(J_2,\varphi_2)\}_3,\alpha(J_1,\varphi_0)\}_3\rho(J_1,J_2,J_3)dJ_1\,dJ_2\,dJ_3\,d\varphi_0. \tag{C1}$$

Performing integration by parts we get

$$R_C^{(2)}(\tau_1,\tau_2)=\int\alpha(J_3,\varphi_3)\{\alpha(J_2,\phi_2),\{\alpha(J_1,\varphi_0),\rho(J_1,J_2,J_3)\}_3\}_3\,dJ_1\,dJ_2\,dJ_3\,d\varphi_0. \tag{C2}$$

Our goal is to find such function $\rho(J_1,J_2,J_3)$, that will not result in divergent derivatives $\partial\alpha(t)/\partial J_j$, and at the same time will not have derivatives $\partial^n\rho/\partial J^n$ higher than first-order ones. The latter is necessary to have discrete spectrum of $R_C^{(2)}(\Omega_1,\Omega_2)$, i.e., in the form of δ-functions. One may notice that the derivative $[(\partial/\partial J_1)+(\partial/\partial J_2)+(\partial/\partial J_3)]$ in brackets $\{A,B\}_3$ does not influence a multiplier of the form $f(aJ_1+bJ_2+cJ_3)$, if $a+b+c=0$. Therefore it is reasonable to look for the expression of $\rho(J_1,J_2,J_3)$ in the form

$$\rho(J_1,J_2,J_3)=f_1(J_1)f_2(a_1J_1+b_1J_2)\times f_3(a_2J_1+b_2J_2+c_2J_3), \tag{C3}$$

where $a_1+b_1=0$, $a_2+b_2+c_2=0$. Substituting this into Eq. (C2) we get

$$\begin{aligned}R_C^{(2)}(\tau_1,\tau_2)=&\int\Bigg(\alpha_3\frac{\partial\alpha_2}{\partial\varphi_0}\left[\frac{\partial}{\partial J_1}\left(\frac{\partial\alpha_1}{\partial\varphi_0}f_1'(J_1)\right)f_2(a_1J_1+b_1J_2)f_3(a_2J_1+b_2J_2+c_2J_3)\right]\\&-\alpha_3\frac{\partial\alpha_2}{\partial J_2}\left[\frac{\partial^2\alpha_1}{\partial\varphi_0^2}f_1'(J_1)f_2(a_1J_1+b_1J_2)f_3(a_2J_1+b_2J_2+c_2J_3)\right]\Bigg)dJ_1\,dJ_2\,dJ_3\,d\varphi_0\\=&\int\Bigg(-\alpha_3\frac{\partial\alpha_2}{\partial\varphi_0}\frac{\partial\alpha_1}{\partial\varphi_0}f_1'(J_1)\frac{\partial}{\partial J_1}(f_2(a_1J_1+b_1J_2)f_3(a_2J_1+b_2J_2+c_2J_3))+\alpha_3\alpha_2\frac{\partial^2\alpha_1}{\partial\varphi_0^2}f_1'(J_1)\\&\times\frac{\partial}{\partial J_2}(f_2(a_1J_1+b_1J_2)f_3(a_2J_1+b_2J_2+c_2J_3))\Bigg)dJ_1\,dJ_2\,dJ_3\,d\varphi_0,\end{aligned} \tag{C4}$$

where in the last step integration by parts was used. After substituting Fourier decomposition $\alpha(J_j,\varphi_j)=\Sigma_n\alpha_n(J_j)e^{in\varphi_j}$ and integrating out φ_0, the last expression in (C4) becomes

$$\begin{aligned}R_C^{(2)}(\tau_1,\tau_2)=&\sum_{n,m}\int dJ_1\,dJ_2\,dJ_3\,2\pi\alpha_m(J_3)\alpha_n(J_2)\alpha_{-m-n}(J_1)(-m-n)f_1'(J_1)\left(\left(n\frac{\partial}{\partial J_1}+(m+n)\frac{\partial}{\partial J_2}\right)\right.\\&\left.\times(f_2(a_1J_1+b_1J_2)f_3(a_2J_1+b_2J_2+c_2J_3))\right)\exp(im\omega(J_3)t_2+in\omega(J_2)t_1).\end{aligned} \tag{C5}$$

We now find such coefficients a_2, b_2, c_2 and a_1, b_1 that $na_2+(n+m)b_2=0$. These coefficients can be chosen as $a_2=-(n+m)$, $b_2=n$, $c_2=m$, $a_1=-1$, $b_1=1$. Finally the distribution density and the response function take the following form:

$$\rho(J_1,J_2,J_3)=f_1(J_1)f_2(J_2-J_1)f_3(mJ_3+nJ_2-(n+m)J_1), \tag{C6}$$

$$\begin{aligned}R_C^{(2)}(\tau_1,\tau_2)=&2\pi\sum_{n,m}\int dJ_1\,dJ_2\,dJ_3\,\alpha_m(J_3)\alpha_n(J_2)\alpha_{-m-n}(J_1)(-m-n)mf_1'(J_1)f_2'(J_2-J_1)\\&\times f_3(mJ_3+nJ_2-(n+m)J_1)\exp(im\omega(J_3)t_2+in\omega(J_2)t_1).\end{aligned} \tag{C7}$$

For the microcanonical distribution density $\rho(J_1,J_2,J_3)$, functions $f_1(J_1)$ and $f_2(J_2-J_1)$ would be δ-functions $\delta(J_1-J_0)$ and $\delta(J_2-J_1)$ correspondingly, which lead to the divergence of the classical response function (C7). Yet, we may impose two uncertainties to the functions $f_1(J_1)$ and $f_2(J_2-J_1)$ replacing δ-functions with the step functions of the width Δ,

$$\begin{aligned} f_1(J_1) &= \frac{1}{\Delta_1}\,\theta((J_1-J_0)+\Delta_1/2)\,\theta(\Delta_1/2-(J_1-J_0)), \\ f_2(J_2-J_1) &= \frac{1}{\Delta_2}\,\theta((J_2-J_1)+\Delta_2/2)\,\theta(\Delta_2/2-(J_2-J_1)). \end{aligned} \tag{C8}$$

This removes the divergence of the classical response function since no derivatives of the δ-function appears in$R_C^{(2)}\times(\tau_1,\tau_2)$. The normalized uncertainty distribution density then has the following form:

$$\begin{aligned} \rho(J_1,J_2,J_3) = {} & \frac{1}{2\pi\Delta_1\Delta_2}\,\theta((J_1-J_0)+\Delta_1/2)\,\theta((\Delta_1/2) \\ & -(J_1-J_0))\times\theta((J_2-J_1) \\ & +\Delta_2/2)\,\theta((\Delta_2/2)-(J_2-J_1)) \\ & \times\delta\left(J_3+\frac{n}{m}J_2-\frac{n+m}{m}J_1\right) \end{aligned} \tag{C9}$$

and the classical response function (C7) becomes

$$\begin{aligned} R_C^{(2)}(\tau_1,\tau_2) = \sum_{n,m}\frac{-(m+n)m}{\Delta_1\Delta_2} \Bigg\{ & \alpha_m(J_3)\,\alpha_n(J_2)\,\alpha_{-m-n}(J_1)\exp(im\omega(J_3)t_2+in\omega(J_2)t_1)\Bigg|_{\substack{J_1=J_0+\Delta_1/2\\ J_2=J_0+\Delta_2/2+\Delta_1/2\\ J_3=J_0+(\Delta_1-\Delta_2(n/m))/2}} \\ & -\alpha_m(J_3)\,\alpha_n(J_2)\,\alpha_{-m-n}(J_1)\exp(im\omega(J_3)t_2+in\omega(J_2)t_1)\Bigg|_{\substack{J_1=J_0-\Delta_1/2\\ J_2=J_0+\Delta_2/2-\Delta_1/2\\ J_3=J_0-(\Delta_1+\Delta_2(n/m))/2}} \\ & -\alpha_m(J_3)\,\alpha_n(J_2)\,\alpha_{-m-n}(J_1)\exp(im\omega(J_3)t_2+in\omega(J_2)t_1)\Bigg|_{\substack{J_1=J_0+\Delta_1/2\\ J_2=J_0-\Delta_2/2+\Delta_1/2\\ J_3=J_0+(\Delta_1+\Delta_2(n/m))/2}} \\ & +\alpha_m(J_3)\,\alpha_n(J_2)\,\alpha_{-m-n}(J_1)\exp(im\omega(J_3)t_2+in\omega(J_2)t_1)\Bigg|_{\substack{J_1=J_0-\Delta_1/2\\ J_2=J_0-\Delta_2/2-\Delta_1/2\\ J_3=J_0-(\Delta_1-\Delta_2(n/m))/2}} \Bigg\}. \end{aligned} \tag{C10}$$

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