Real-time path-integral approach to quantum coherence and dephasing in nonadiabatic transitions and nonlinear optical response

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Quantum coherence and its destruction (dephasing) by coupling to a dissipative environment plays an important role in time-resolved nonlinear optical response as well as nonadiabatic transitions and tunneling processes in condensed phases. Generating functions of density-matrix elements and multitime coordinate and momentum correlation functions related to these phenomena are calculated using a path-integral approach by performing functional integration. The dissipative environment is assumed to be an ensemble of harmonic oscillators and is taken into account by using Feynman-Vernon influence functional. Closed-form expressions for generating functions in terms of the bath spectral density are derived. The present theory generalizes earlier calculations of these quantities to arbitrary temperatures, any dependence of the transition coupling on coordinates (non-Condon effects), and arbitrary order in the interstate coupling. Conditions for factorizing the Liouville-space generating functions that allow a reduced description based on the classical Langevin equation are established. Possible applications to four-wave-mixing spectroscopy and nonadiabatic rate processes are discussed.

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I. INTRODUCTION

Dephasing processes are crucial in the dynamics of optical processes and curve crossing (nonadiabatic transitions) in condensed phases. Dephasing takes place whenever a quantum system is prepared in an off-resonant element of the density matrix which carries a phase (coherence). That phase can be affected by coupling to other degrees of freedom, which may result in the loss of coherence (dephasing) [1–4].

In this article we consider a model Hamiltonian commonly used in the description of nonlinear-optical response [5–7], nonadiabatic transitions [8–15] tunneling [16,17], Josephson junction [18], etc. We derive closed-form expressions for Liouville-space generating functions which represent the density matrix of the reduced system, and are essential in the theoretical description of these phenomenon. The primary quantum system in taken to be a two-level system with a ground state $|g\rangle$ and an excited state $|e\rangle$, and its Hamiltonian is given by

$$H_S = H_0 + E(t)H_I \ , \tag{1.1}$$

where

$$H_0 = |g\rangle H_g \langle g| + |e\rangle H_e \langle e| \ , \tag{1.2}$$

with

$$\begin{aligned} H_g &= \frac{p^2}{2M} + U_g(q) \ , \\ H_e &= \frac{p^2}{2M} + U_e(q) \ , \end{aligned} \tag{1.3}$$

and p, q, and M represent the momentum, the coordinate, and the mass, respectively. The interaction consists of the time-dependent function $E(t)$ and the operator H_I, which is given by

$$H_I = |g\rangle V(p,q) \langle e| + |e\rangle V^*(p,q) \langle g| \ , \tag{1.4}$$

where $V(p,q)$ is any function of the coordinate and the momentum. In nonadiabatic curve crossing problems, $E(t)=1$ and $V(p,q)$ represents the nonadiabatic interaction between the two states $|e\rangle$ and $|g\rangle$. In optical problems $E(t)$ and $V(p,q)=\mu(q)$ represent the radiation field and the dipole interaction between the two states, respectively. The potentials of the excited and ground states are assumed to be harmonic (see Fig. 1):

$$\begin{aligned} U_g(q) &= \tfrac{1}{2} M \omega_0^2 q^2 \ , \\ U_e(q) &= \tfrac{1}{2} M \omega_0^2 (q+D)^2 + \hbar\omega_{eg} \ . \end{aligned} \tag{1.5}$$

This system is a direct product of a two-level system and a single harmonic coordinate. The choice of harmonic potentials in this paper allows the incorporation of a general model of the dissipative medium with an arbitrary spectral density and temperature. By restricting the model for dissipation it is possible to treat general anhar-

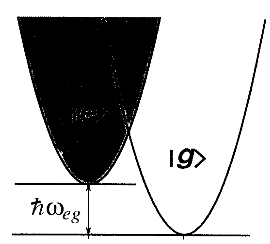

FIG. 1. Potential surfaces of the linearly displaced harmonic-oscillator system. The lower state is denoted by $|g\rangle$, the upper by $|e\rangle$. The equilibrium coordinate displacement and the energy difference between two potential are expressed by D and $\hbar\omega_{eg}$, respectively.

monic potentials. This will be discussed in Sec. VI. Since the potentials of the system are harmonic, we may easily study its dynamics by expanding the wave function perturbatively in the interaction. However, if the system is further coupled to a dissipative environment, such as phonons, the solvent, polarization fluctuations, etc., its dynamics should be described using the density matrix in Liouville space rather than the wave function. The density matrix allows a proper description of quantum coherence and dephasing processes which play an important role in the presence of dissipation.

Yan and Mukamel have developed a semiclassical Liouville-space generating function procedure for the propagation of the density matrix with dissipation [19,20]. Applications were made to four wave mixing spectroscopies. Semiclassical approximations were obtained by expressing the density matrix using the Wigner representation. In a pump-probe measurement, for example, the approach allows the introduction of a doorway state and a window state which are wave packets in Liouville space and provide a physical picture for the process. Another application to electron transfer in a polar medium resulted in an expression for the rate that interpolates between the adiabatic and nonadiabatic limits [12]. Quantum tunneling via superexchange was also treated using the same approach [21]. The potentials U_g and U_e used in the work of Yan and Mukamel are in general anharmonic and the dissipation was incorporated using a Langevin equation, generalized to include quantum coherence (off-diagonal elements of the density matrix). Although the system was treated quantum mechanically, the inclusion of a classical Langevin force necessarily limits the applicability of this procedure to high temperatures. This could be seen by calculating the linear absorption line shape and comparing it with the exact expression obtained using the fluctuation-dissipation theorem [see Eqs. (C7)–(C9)]. Both expressions agree at high temperatures and differ at lower temperatures. The difference at low temperatures may be attributed to the classical Langevin approach. If we use the quantum Langevin force [22], the low-temperature behavior of the line-shape function may be improved; however, this is not enough. The system and the environment interact and the environment carries the memory of the interaction. This effect often denoted the "memory effect" or the "correlated effect" of the environment [3] is particularly important at low temperatures where thermal fluctuations get smaller and the reaction of the heat bath to the system becomes important. To take this effect into account, we must explicitly consider the environment degrees of freedom instead of introducing them via the random force. There are several ways to treat the environment. For a harmonic system, the path-integral method is a powerful approach. The environment is assumed to be an ensemble of harmonic oscillators which may be eliminated using the Feynman-Vernon influence functional [23]. Numerous studies have been carried out using the real-time path-integral formalism and the influence functional [2,24–26]. A comprehensive study of a harmonic system was performed by Grabert, Schramm, and Ingold [3]. They evaluated the functional integral of the system using the minimal path of the action including the correlated effect of the environment. The density matrix, as well as coordinate and momentum correlation functions were obtained, and the time evolution of a factorized initial state was studied as an example of the relaxation of nonequilibrium initial states.

In this paper we use real-time path integrals to develop a fully microscopic closed-form expression for dynamical variables related to the evolution of the density matrix for the system described by Eqs. (1.1)–(1.5) coupled to a dissipative medium. We extend the results of Grabert *et al.* which were restricted to a single-harmonic-oscillator potential, to the present problem by introducing a phase force, which is associated with the quantum coherence between the excited state and the ground state. We derive Liouville-space generating functions (LGF's) which allow us to evaluate the density matrix as well as coordinate and momentum correlation functions to arbitrary order in the interaction. The limitations of the classical Langevin approach are precisely specified. In addition to the microscopic treatment of dissipation which applies to all temperatures, our results generalize the earlier work of Yan and Mukamel in other important aspects. Our generating function applies to an arbitrary dependence of the nonadiabatic coupling on coordinates and momenta, i.e., non-Condon effects in optical line shapes and a coordinate-dependent nonadiabatic coupling. In addition, we provide closed-form expressions for multitime correlation functions of arbitrary order. The work of Yan and Mukamel involved the Condon approximation and considered second- and fourth-order correlation functions. On the other hand, that work is more general in other respects, since it provided a semiclassical description for arbitrary anharmonic potentials, and in the absence of damping resulted in an exact expression for the LGF for general harmonic potentials where the U_g and U_e potentials have a displaced equilibrium position as well as a different frequency.

The organization of this paper is as follows: In Sec. II, we develop the concept of the phase force after introducing the influence functional for the effect of the environment, and evaluate the density matrix of the system. In Sec. III we calculate the LGF which can be used to study the time evolution of the system with an arbitrary coordinate and momentum dependence of the nonadiabatic coupling, and evaluate multitime coordinate-momentum correlation functions. In Sec. IV we calculate generating functions of the density matrix to even order in the interaction H_I. These quantities are also relevant for spectroscopies with non-Condon dipole interactions. In Sec. V we connect our results to these problems. In Sec. VI we discuss the conditions for factorizing the LGF and the density matrix, and establish the relation between our results and the semiclassical Langevin equation. Section VII is devoted to discussion and concluding remarks.

II. LIOUVILLE-SPACE PATHS FOR A COORDINATE-INDEPENDENT NONADIABATIC COUPLING

Let us assume that the system [Eqs. (1.1)–(1.5)] is coupled to an environment consisting of a set of harmonic oscillators with coordinates x_n and momenta p_n. The interaction between the system and the nth oscillator is assumed to be linear with a coupling strength c_n. The total Hamiltonian is then given by

$$H=H_s+H' , \tag{2.1}$$

where

$$H'=\sum_n \left[\frac{p_n^2}{2m_n}+\frac{m_n\omega_n^2}{2}\left[x_n-\frac{c_n q}{m_n\omega_n^2}\right]^2\right] . \tag{2.2}$$

We have followed the common notation of Grabert, Schramm, and Ingold [3]. The total system is assumed to be initially at equilibrium in the ground electronic state:

$$\rho_g=\frac{|g\rangle\langle g|\exp[-\beta(H_g+H')]}{\mathrm{Tr}\{\exp[-\beta(H_g+H')]\}} , \tag{2.3}$$

where $\beta\equiv 1/k_BT$ is the inverse temperature. Since we are not interested in the dynamics of the environment, we trace over its coordinates. We thus introduce the reduced density matrix

$$\rho(t)\equiv \mathrm{Tr}_B[\rho_{\mathrm{tot}}(t)] . \tag{2.4}$$

Here, $\mathrm{Tr}_B[\ ]$ represents the trace over the environment (the bath) degrees of freedom and $\rho_{\mathrm{tot}}(t)$ is the total (system plus bath) density matrix. By expanding the reduced density matrix of the system $\rho(t)$, in orders of the interaction H_I, we have

$$\rho(t)=\sum_{n=0}^{\infty}\int_0^t d\tau_n\int_0^{\tau_n}d\tau_{n-1}\cdots\int_0^{\tau_2}d\tau_1 E(\tau_n)E(\tau_{n-1})\cdots E(\tau_1)\rho^{(n)}(t,\tau_n,\tau_{n-1},\ldots,\tau_1) , \tag{2.5}$$

where

$$\rho^{(n)}(t,\tau_n,\tau_{n-1},\ldots,\tau_1)=\left[-\frac{i}{\hbar}\right]^n \mathrm{Tr}_B\left[\exp\left[-\frac{i}{\hbar}(t-\tau_n)(H_0+H')^{\times}\right]H_I^{\times}\exp\left[-\frac{i}{\hbar}(\tau_n-\tau_{n-1})(H_0+H')^{\times}\right]\right.$$
$$\left.\times H_I^{\times}\ldots H_I^{\times}\exp\left[-\frac{i}{\hbar}(\tau_2-\tau_1)(H_0+H')^{\times}\right]H_I^{\times}\rho_g\right] . \tag{2.6}$$

In the above we used the superoperator notation $\times$ defined by

$$A^{\times}B\equiv AB-BA ,$$
$$A^{\times}B^{\times}C\equiv A(BC-CB)-(BC-CB)A , \tag{2.7}$$

and so forth, where A, B, and C are ordinary operators. Since each $H_I^{\times}$ can act either from the left or from the right, and since $\rho^{(n)}$ contains $nH_I^{\times}$ factors, Eq. (2.6) naturally separates into $N=2^n$ terms denoted *Liouville-space paths* [1]. In practice we need to evaluate only half of these terms, since they always come in Hermitian conjugate pairs, and $\rho^{(n)}$ are Hermitian. We thus have

$$\rho^{(n)}(t,\tau_n,\tau_{n-1},\ldots,\tau_1)=\sum_{\alpha=1}^{N/2}\rho_\alpha^{(n)}(t)+\mathrm{H.c.} , \tag{2.8}$$

where α labels the paths. The function $\rho_\alpha^{(n)}(t)$ represents the contributions of the αth Liouville-space path to the density matrix evaluated to nth order in H_I, and will be denoted the *Liouville-space generating functions.* In Sec. III we shall generalize this definition to allow for several interruptions of the paths by other perturbations [see Eq. (3.1)]. Note that the LGF, $\rho_\alpha^{(n)}(t)$, depends on all time variables τ_n and not just on t. The τ_n dependence is incorporated in the α subscript, since each path α represents a specific choice of the time arguments. For $n=2$, for example, there are two possible Liouville-space paths plus their Hermitian conjugates. These can be represented using double-sided Feynman diagrams, as shown in Fig. 2., and are defined as

$$\rho_1^{(2)}(t)\equiv \mathrm{Tr}_B[G_1^{(2)}(t,\tau_2)V(p,q)G_1^{(2)}(\tau_2,\tau_1)\times V^*(p,q)G_1^{(2)}(\tau_1,0)\rho_g]$$
$$=\mathrm{Tr}_B[G_{gg}(t,\tau_2)V(p,q)G_{eg}(\tau_2,\tau_1)\times V^*(p,q)G_{gg}(\tau_1,0)\rho_g] \tag{2.9}$$

and

$$\rho_2^{(2)}(t)\equiv \mathrm{Tr}_B\{G_2^{(2)}(t,\tau_2)\{[G_2^{(2)}(\tau_2,\tau_1)V^*(p,q)G_2^{(2)}(\tau_1,0)\rho_g]V(p,q)\}\}$$
$$=\mathrm{Tr}_B\{G_{ee}(t,\tau_2)\{[G_{eg}(\tau_2,\tau_1)V^*(p,q)G_{gg}(\tau_1,0)\rho_g]V(p,q)\}\} , \tag{2.10}$$

where $G_\alpha^{(n)}(\tau,\tau')$ refer the propagation operators corresponding to the paths shown in Fig. 2, and $G_{nm}(\tau,\tau')$ is defined by

$$G_{nm}(\tau,\tau')A\equiv \exp[-i(\tau-\tau')(H_n+H')/\hbar]A\exp[i(\tau-\tau')(H_m+H')/\hbar] . \tag{2.11}$$

For clarity hereafter in this section we consider the simple case whereby $V(p,q)=\mathrm{const}$, which does not depend on the coordinate or the momentum. This assumption will be relaxed in Sec. IV.

In the path-integral formalism, each of the Liouville-space paths can be expressed as

$$\rho_\alpha^{(n)}(q_f,q_f',t)=\int dq_i \int dq_i' \int_{q(0)=q_i}^{q(t)=q_f} D[q] \int_{q'(0)=q_i'}^{q'(t)=q_f'} D[q'] \rho_g^{\rm CS}(q,q';q_i,q_i') \times \exp\left[\frac{i}{\hbar}S_L[q;t,0]\right] F[q,q';t,0] \exp\left[-\frac{i}{\hbar}S_R[q';t,0]\right] . \quad (2.12)$$

The actions S_L and S_R are defined by

$$S_L[q;t,0]=\int_0^t ds[\tfrac{1}{2}M\dot{q}^2-U_L(q,s)] ,$$
$$S_R[q';t,0]=\int_0^t ds[\tfrac{1}{2}M\dot{q}'^2-U_R(q',s)] , \quad (2.13)$$

respectively, where U_L and U_R are the potentials of the left-hand side (ket) and the right-hand side (bra) of the density matrix. The various Liouville-space paths simply differ by the specific choices of U_L and U_R. As an example, the potentials for the paths corresponding to Fig. 2 are given in Table I. By introducing these potentials, we can derive a single formal expression which will hold for all paths. The Feynman-Vernon influence functional $F[q,q';0,t]$ is written as [23]

$$F[q,q';t,0]=\exp\left[-\frac{iM}{\hbar}\int_0^t ds[q(s)-q'(s)]\frac{d}{ds}\int_0^s du\, \gamma(s-u)\left[\frac{q(u)+q'(u)}{2}\right] -\frac{1}{2\hbar}\int_0^t ds\int_0^t du\, K'(s-u)[q(s)-q'(s)][q(u)-q'(u)]\right] , \quad (2.14)$$

where

$$\gamma(s)=\frac{2}{M}\int_0^\infty \frac{d\omega}{\pi}\frac{J(\omega)}{\omega}\cos(\omega s) , \quad (2.15)$$

and

$$K'(s)=\int_0^\infty \frac{d\omega}{\omega}J(\omega)\coth\left[\frac{\omega\hbar\beta}{2}\right]\cos(\omega s) , \quad (2.16)$$

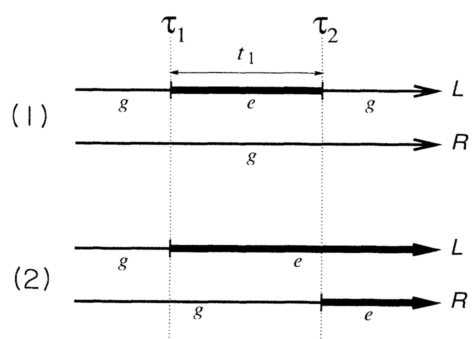

FIG. 2. Double-sided Feynman diagrams in second order. The lines denoted by L and R represent the time evolution of the left- (ket) and the right- (bra) hand sides of the density matrix, respectively. The thin and thick lines denote the ground state $|g\rangle$ and the excited state $|e\rangle$. Path 1 corresponds the transition from g to g, whereas path 2 corresponds the transition from g to e. Two other paths, which are the Hermitian conjugates of the above paths, are not shown. These conjugate paths can be obtained by interchanging L and R.

with the spectral distribution function of the coupling,

$$J(\omega)=\pi\sum_n \frac{c_n^2}{2m_n\omega_n}\delta(\omega-\omega_n) . \quad (2.17)$$

The initial condition and the initial correlation between the system and the environment are incorporated into the function $\rho_g^{\rm CS}(q,q';q_i,q_i')$, where CS stands for the correlated state [3]. This is not only a function of q_i and q_i', but is also a functional of the trajectories $q(t)$ and $q'(t)$ and is presented in Appendix A.

We now introduce the center and the difference coordinates

$$r\equiv\frac{q+q'}{2}, \quad x\equiv q-q' . \quad (2.18)$$

The initial and the final coordinates x_i, r_i and r_f, x_f are defined similarly. Then the density-matrix element Eq. (2.12) is rewritten as

TABLE I. Potentials of the left- (ket) and right- (bra) hand sides of the density matrix corresponding to the Liouville-space paths given in Fig. 2.

α	$U(q,s)$	$0-\tau_1$	$\tau_1-\tau_2$	τ_2-t
1	$U_L(q,s)$	$U_g(q)$	$U_e(q)$	$U_g(q)$
	$U_R(q',s)$	$U_g(q')$	$U_g(q')$	$U_g(q')$
2	$U_L(q,s)$	$U_g(q)$	$U_e(q)$	$U_e(q)$
	$U_R(q',s)$	$U_g(q')$	$U_g(q')$	$U_e(q')$

$$\rho_\alpha^{(n)}(x_f,r_f,t)=\int dx_i \int dr_i \int_{x(0)=x_i}^{x(t)=x_f} D[x] \int_{r(0)=r_i}^{r(t)=r_f} D[r] \exp\left[\frac{i}{\hbar}\Sigma_t[x,r,t;x_i,r_i,0]\right] \exp\left[-\frac{1}{\hbar}\Sigma_\beta(x_i,r_i)\right], \tag{2.19}$$

where the subscript β implies that this quantity depends on temperature and

$$\Sigma_\beta(x_i,r_i)=M\left[\frac{1}{2\Lambda}r_i^2+\frac{\Omega}{2}x_i^2\right], \tag{2.20}$$

and

$$\begin{aligned}\Sigma_t[x,r,t;x_i,r_i,0]=&M\int_0^t ds[r_iC_1(s)-ix_iC_2(s)]x(s)+\frac{i}{2}M\int_0^t ds\int_0^t du\, R'(s,u)x(s)x(u)\\&+\int_0^t ds\, M\left[\dot{x}(s)\dot{r}(s)-\omega_0^2x(s)r(s)-x(s)\frac{d}{ds}\int_0^s du\,\gamma(s-u)r(u)\right]\\&+\frac{i}{2}\int_0^t ds\int_0^t du\, K'(s-u)x(s)x(u)+\int_0^t ds[F_\alpha^{(n)}(s)x(s)+f_\alpha^{(n)}(s)r(s)+\Phi_\alpha^{(n)}(s)]\,. \end{aligned}\tag{2.21}$$

In the above equation, $K'(s-u)$ is defined by Eq. (2.16), and $C_1(s)$, $C_2(s)$, and $R'(s,u)$ are related to the correlated state and are given by Eqs. (A3) and (A4) in Appendix A. The temperature-dependent parameters Λ and Ω are expressed in the Matsubara frequency $\nu_n=2\pi n/\hbar\beta$ as

$$\begin{aligned}\Lambda&=\frac{1}{\hbar\beta}\sum_{n=-\infty}^{\infty}\frac{1}{\omega_0^2+\nu_n^2+|\nu_n|\hat{\gamma}(|\nu_n|)}\,,\\ \Omega&=\frac{1}{\hbar\beta}\sum_{n=-\infty}^{\infty}\frac{\omega_0^2+|\nu_n|\hat{\gamma}(|\nu_n|)}{\omega_0^2+\nu_n^2+|\nu_n|\hat{\gamma}(|\nu_n|)}\,,\end{aligned}\tag{2.22}$$

respectively, where $\hat{\gamma}(z)$ is the Laplace transform of $\gamma(s)$,

$$\hat{\gamma}(z)=\int_0^\infty ds\,\gamma(s)\exp(-zs)\,. \tag{2.23}$$

The functions $F_\alpha^{(n)}(s)$, $f_\alpha^{(n)}(s)$, and $\Phi_\alpha^{(n)}(s)$ depend on the path α, and are defined by

$$\begin{aligned}F_\alpha^{(n)}(s)&=-\left[\frac{d}{dx}[U_L(r+x/2,s)-U_R(r-x/2,s)]\right]\Bigg|_{x=r=0},\\ f_\alpha^{(n)}(s)&=-\left[\frac{d}{dr}[U_L(r+x/2,s)-U_R(r-x/2,s)]\right]\Bigg|_{x=r=0},\\ \Phi_\alpha^{(n)}(s)&=-[U_L(r+x/2,s)-U_R(r-x/2,s)]|_{x=r=0}\,.\end{aligned}\tag{2.24}$$

As an example, we present the functions corresponding to the paths of Fig. 2 in Table II. In Eq. (2.21), because of the quantum coherence between the bra and the ket of the density matrix, we have not only the contribution from the real force $F_\alpha^{(n)}(s)$, but also the phase force $f_\alpha^{(n)}(s)$ and the phase $\Phi_\alpha^{(n)}(s)$. In spite of the existence of the phase force, our system is still harmonic, and only the minimal path of the action contributes to the functional integration of Eq. (2.19). The minimal path is the solution of the equation of the motion:

$$\begin{aligned}\ddot{r}+\frac{d}{ds}\int_0^s du\,\gamma(s-u)r(u)+\omega_0^2r&=\frac{1}{M}F_\alpha^{(n)}(s)+\frac{i}{M}\int_0^t du\,K'(s-u)x(u)\\&\quad+[r_iC_1(s)-ix_iC_2(s)]\\&\quad+i\int_0^t du\,R'(s,u)x(u)\,,\end{aligned}\tag{2.25}$$

where $x(s)$ is the solution of

$$\ddot{x}-\frac{d}{ds}\int_s^t du\,\gamma(u-s)x(u)+\omega_0^2x=\frac{1}{M}f_\alpha^{(n)}(s)\,, \tag{2.26}$$

and $C_1(s)$, $C_2(s)$, and $R'(s,u)$ are auxiliary functions related to the correlated state and are given by Eqs. (A3) and (A4) in Appendix A. The above equations are readily obtained from the phase Eq. (2.21) by taking the variation of $x(s)$ and $r(s)$. Equation (2.25) with Eq. (2.26) extend the quantum Langevin equation [22] to incorporate the correlated state and the phase force $f_\alpha^{(n)}(s)$. Except for the phase force $f_\alpha^{(n)}(s)$, the following procedure is parallel to Ref. [3] and we obtain the propagation function in the form

TABLE II. Functions $F_\alpha^{(2)}(s)$, $f_\alpha^{(2)}(s)$, and $\Phi_\alpha^{(2)}(s)$ for the paths given in Fig. 2, where we introduced $\lambda=MD^2\omega_0^2/2\hbar$ and $\xi=MD\omega_0^2/\hbar$.

α	functions	$0-\tau_1$	$\tau_1-\tau_2$	τ_2-t
1	$F_1^{(2)}(s)$	0	$-\hbar\xi/2$	0
	$f_1^{(2)}(s)$	0	$-\hbar\xi$	0
	$\Phi_1^{(2)}(s)$	0	$-\hbar(\omega_{eg}+\lambda)$	0
2	$F_2^{(2)}(s)$	0	$-\hbar\xi/2$	$-\hbar\xi$
	$f_2^{(2)}(s)$	0	$-\hbar\xi$	0
	$\Phi_2^{(2)}(s)$	0	$-\hbar(\omega_{eg}+\lambda)$	0

$$\exp\left[\frac{i}{\hbar}\Sigma_t(x_f,r_f,t;x_i,r_i,0)\right]\equiv\int_{x(0)=x_i}^{x(t)=x_f}D[x]\int_{r(0)=r_i}^{r(t)=r_f}D[r]\exp\left[\frac{i}{\hbar}\Sigma_t[x,r,t;x_i,r_i,0)\right]$$
$$=\frac{1}{N(t)}\exp[i\alpha(t)r_ix_i+i\beta(t)r_ix_f+i\delta(t)r_i-\epsilon(t)x_i^2+i\phi(t)x_ir_f$$
$$+i\psi(t)x_ix_f+\zeta(t)x_i+\kappa(t)x_f+i\sigma(t)r_f+i\tau(t)x_fr_f+c'(t)+ic''(t)]\ , \qquad (2.27)$$

where the functions and the outline of calculations are given in Appendix B. The propagation function in Eq. (2.19), which was defined in terms of a functional of $x(t)$ and $r(t)$, is now a function of x_f, r_f, x_i, r_i, and t. Then, by integrating Eq. (2.27) over x_i and r_i, with $\exp[-\Sigma_\beta(x_i,r_i)/\hbar]$, we can recast the density matrix in the Gaussian form:

$$\rho_\alpha^{(n)}(x,r,t)=\left[\frac{1}{2\pi\langle q^2\rangle_g}\right]^{1/2}\times\exp\left[-\frac{1}{2\langle q^2\rangle_g}(r-\langle\bar r_t\rangle_\alpha^{(n)})^2-\frac{1}{2\hbar}\langle p^2\rangle_g x^2+\frac{1}{\hbar}\langle\bar p_t\rangle_\alpha^{(n)}x+Q_\alpha^{(n)}(t)\right]. \qquad (2.28)$$

The position and the momentum expectation values are defined by

$$\langle\bar r_t\rangle_\alpha^{(n)}\equiv \mathrm{Tr}[\hat r\rho_\alpha^{(n)}(t)]/\mathrm{Tr}[\rho_\alpha^{(n)}(t)]\ ,$$
$$\langle\bar p_t\rangle_\alpha^{(n)}\equiv \mathrm{Tr}[\hat p\rho_\alpha^{(n)}(t)]/\mathrm{Tr}[\rho_\alpha^{(n)}(t)]\ , \qquad (2.29)$$

respectively. These time-dependent parameters and the overall phase $Q_\alpha^{(n)}(t)$ can be expressed in terms of the antisymmetrized position correlation function (the response function) and the symmetrized position correlation function of the ground equilibrium state:

$$\chi(t)\equiv\frac{i}{\hbar}\langle q(t)q-qq(t)\rangle_g$$
$$=\frac{1}{M}\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\frac{\omega\tilde\gamma(\omega)}{(\omega_0^2-\omega^2)^2+\omega^2\tilde\gamma^2(\omega)}\sin(\omega t)\ , \qquad (2.30)$$

and

$$S(t)\equiv\frac{1}{2}\langle q(t)q+qq(t)\rangle_g$$
$$=\frac{\hbar}{M}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{\omega\tilde\gamma(\omega)}{(\omega_0^2-\omega^2)^2+\omega^2\tilde\gamma^2(\omega)}\times\coth\left[\frac{\beta\hbar\omega}{2}\right]\cos(\omega t)\ , \qquad (2.31)$$

with

$$\tilde\gamma(\omega)\equiv\hat\gamma(-i\omega)J(\omega)/\omega\ , \qquad (2.32)$$

in the form

$$\langle\bar r_t\rangle_\alpha^{(n)}=\int_0^t dt'\chi(t-t')F_\alpha^{(n)}(t')+\frac{i}{\hbar}\int_0^t dt'S(t-t')f_\alpha^{(n)}(t')\ , \qquad (2.33)$$

$$\langle\bar p_t\rangle_\alpha^{(n)}=M\int_0^t dt'\dot\chi(t-t')F_\alpha^{(n)}(t')+\frac{iM}{\hbar}\int_0^t dt'\dot S(t-t')f_\alpha^{(n)}(t')\ , \qquad (2.34)$$

$$Q_\alpha^{(n)}(t)=\frac{i}{\hbar}\int_0^t dt'\left[\Phi_\alpha^{(n)}(t')+f_\alpha^{(n)}(t')\times\int_0^{t'}dt''\chi(t'-t'')F_\alpha^{(n)}(t'')\right]-\frac{1}{2\hbar^2}\int_0^t dt'\int_0^t dt''f_\alpha^{(n)}(t')f_\alpha^{(n)}(t'')S(t'-t'')\ , \qquad (2.35)$$

and

$$\langle q^2\rangle_g=\frac{\hbar}{M}\Lambda=S(0)\ ,$$
$$\langle p^2\rangle_g=\hbar M\Omega=-M^2\ddot S(0)\ . \qquad (2.36)$$

Note that $\chi(t)$ is related to $S(t)$ by the fluctuation-dissipation theorem and $\chi(-t)=-\chi(t)$ and $S(-t)=S(t)$. The first terms of Eqs. (2.33) and (2.34) represent the contributions from the real force $F_\alpha^{(n)}(t)$ and satisfy a linear-response relation with $F_\alpha^{(n)}(t)$ and the response function $\chi(t)$ or its time derivative $\dot\chi(t)$ [3]. The second terms of Eqs. (2.33) and (2.34) are imaginary and represent the contributions from the phase force $F_\alpha^{(n)}(t)$. The second terms have similar form to the linear-response relation, except that the response function $\chi(t)$ is replaced by the symmetrized function $S(t)$. Note that $\langle\bar r_t\rangle^{(n)}=\Sigma_\alpha\langle\bar r_t\rangle_\alpha^{(n)}$ and $\langle\bar p_t\rangle^{(n)}=\Sigma_\alpha\langle\bar p_t\rangle_\alpha^{(n)}$ are real, since they represent the expectation values of Hermitian operations. If we set $f_\alpha^{(n)}(t)=\Phi_\alpha^{(n)}(t)=0$, Eq. (2.28) reduces to the density matrix of a harmonic system driven by the external force $F_\alpha^{(n)}(t)$. When the force $f_\alpha^{(n)}(t)$ and the phase $\Phi_\alpha^{(n)}(t)$ are added, the above result still retains the harmonic form, and the widths of the wave packet $\langle q^2\rangle_g$ and $\langle p^2\rangle_g$ are independent on time. The function $Q_\alpha^{(n)}(t)$ depends on $F_\alpha^{(n)}(t)$, $f_\alpha^{(n)}(t)$, and $\Phi_\alpha^{(n)}(t)$. This function remains in Eq. (2.28) even when we take a trace; i.e.,

$$\mathrm{Tr}[\rho_\alpha^{(n)}(x,r,t)]\equiv\int dr\,\rho_\alpha^{(n)}(0,r,t)$$
$$=\exp[Q_\alpha^{(n)}(t)]\ . \qquad (2.37)$$

In the Wigner representation defined by

$$W(p,q,t) \equiv \frac{1}{2\pi\hbar} \int dx\, e^{-ipx/\hbar} \rho(x,q,t) \; , \tag{2.38}$$

Eq. (2.28) becomes

$$W_\alpha^{(n)}(p,q,t) = \frac{1}{2\pi} \left[\frac{1}{\langle p^2 \rangle_g \langle q^2 \rangle_g} \right]^{1/2} \times \exp \left[-\frac{1}{2\langle q^2 \rangle_g} (q - \langle \bar{q}_t \rangle_\alpha^{(n)})^2 - \frac{1}{2\langle p^2 \rangle_g} (p - \langle \bar{p}_t \rangle_\alpha^{(n)})^2 + Q_\alpha^{(n)}(t) \right] . \tag{2.39}$$

The Wigner function is not positive definite, however, it is extremely useful for comparison with results based on the classical density matrix in phase space and for developing semiclassical approximation for anharmonic systems.

III. LIOUVILLE-SPACE GENERATING FUNCTIONS AND CORRELATION FUNCTIONS WITH ARBITRARY NONADIABATIC INTERACTIONS

A. Liouville-space generating functions

In the previous section, we derived expressions for density matrix elements for constant coupling $V(p,q)=\text{const}$. Here we generalize these results for a coupling of the form $V(p,q)=\mu(q)\eta(p)$, where $\mu(q)$ and $\eta(p)$ are any functions of q and p, respectively. Our goal is to calculate the LGF [Eq. (2.8)] for this model. In fact we shall generalize the definition of the LGF to the form

$$\sigma_\alpha^{(n)}(x,r,t) = \mathrm{Tr}_B[\cdots \mu(q_\alpha^{(n)}(\tau_l))\eta(p_\alpha^{(n)}(\tau_m)) \cdots \times \rho_g \cdots \eta^*(p'^{(n)}_\alpha(\tau_{m'})) \times u^*(q'^{(n)}_\alpha(\tau_{n'})) \cdots] \; , \tag{3.1}$$

which is more general than the LGF introduced previously, since it allows the introduction of arbitrary couplings at any point during the time evolution of the density matrix. Since the derivation requires the introduction of many auxiliary quantities, we shall hereafter proceed gradually. We first evaluate simple quantities including only a single $V(q)$ operator. The generalization to Eq. (3.1) is then straightforward.

Consider a LGF with a coordinate-dependent interaction acting on its ket which is defined by

$$\sigma_\alpha^{(n)}(x,r,t) \equiv \mathrm{Tr}_B[\mu(q_\alpha^{(n)}(\tau))\rho_g] \equiv \mathrm{Tr}_B[G_\alpha^{(n)}(t,\tau)\mu(\hat{q})G_\alpha^{(n)}(\tau,0)\rho_g] \; , \tag{3.2}$$

where $G_\alpha^{(n)}(t,0)$ is the Green function of the total system corresponding to the nth order path labeled α [see Eq. (2.10)]. In the path-integral formalism, this is expressed as

$$\sigma_\alpha^{(n)}(x_f,r_f,t) \equiv \int dx_i \int dr_i \int_{x(0)=x_i}^{x(t)=x_f} D[x] \int_{r(0)=r_i}^{r(t)=r_f} D[r] \mu[r(\tau)+x(\tau)/2] \exp\left[\frac{i}{\hbar}\Sigma_t[x,r;t;x_i,r_i,0] - \frac{1}{\hbar}\Sigma_\beta(x_i,r_i) \right]$$
$$= \left[\mu(\partial/\partial a) \int dx_i \int dr_i \int_{x(0)=x_i}^{x(t)=x_f} D[x] \int_{r(0)=r_i}^{r(t)=r_f} D[r] \exp\left[a\int_0^t ds\, \delta(s-\tau)[r(s)+x(s)/2] + \frac{i}{\hbar}\Sigma_t[x,r;t;x_i,r_i,0] - \frac{1}{\hbar}\Sigma_\beta(x_i,r_i) \right] \right] \Bigg|_{a=0} , \tag{3.3}$$

where the functions are given in Eqs. (2.19)–(2.24). By comparing with Eq. (2.21), we find that the terms proportional to a can be included in the forces by replacing

$$F_\alpha^{(n)}(s) \rightarrow F_\alpha^{(n)}(s) - \frac{ia\hbar}{2}\delta(s-\tau) \; , \quad f_\alpha^{(n)}(s) \rightarrow f_\alpha^{(n)}(s) - ia\hbar\delta(s-\tau) \; . \tag{3.4}$$

Thus, by substituting the above functions into Eq. (2.28), we obtain

$$\sigma_\alpha^{(n)}(x,r,t) = \left[\mu\left[\frac{\partial}{\partial a}\right] \Xi_\alpha^{(n)}(x,r,t,a) \right] \Bigg|_{a=0} , \tag{3.5}$$

where the generating function $\Xi_\alpha^{(n)}(x,r,t,a)$ is expressed as

$$\Xi_\alpha^{(n)}(x,r,t,a) = \left[\frac{1}{2\pi\langle q^2 \rangle_g} \right]^{1/2} \exp\left[\frac{1}{2\langle q^2 \rangle_g}[r - \langle \bar{r}_t \rangle_\alpha^{(n)} - aC(t-\tau)]^2 - \frac{1}{2\hbar}\langle p^2 \rangle_g x^2 + \frac{1}{\hbar}[\langle \bar{p}_t \rangle_\alpha^{(n)} + aM\dot{C}(t-\tau)]x + Q_\alpha^{(n)}(t) + a\langle \bar{q}_t(\tau) \rangle_\alpha^{(n)} + \frac{a^2}{2}C(0) \right] . \tag{3.6}$$

In which $\langle \bar{r}_t \rangle_\alpha^{(n)}$, $\langle \bar{p}_t \rangle_\alpha^{(n)}$, $Q_\alpha^{(n)}(t)$, etc. are given in Sec. II and we defined

$$C(t) \equiv S(t) - i\frac{\hbar}{2}\chi(t) = \langle q(t) q \rangle_g \ , \tag{3.7}$$

and

$$\begin{aligned} \langle \bar{q}_t(\tau) \rangle_\alpha^{(n)} = & \int_0^\tau \chi(\tau - t') F_\alpha^{(n)}(t') dt' \\ & -\tfrac{1}{2}\int_\tau^t dt' \chi(\tau - t') f_\alpha^{(n)}(t') \\ & + \frac{i}{\hbar}\int_0^t dt' S(\tau - t') f_\alpha^{(n)}(t') \ . \end{aligned} \tag{3.8}$$

Note that the last two terms of Eq. (3.8) are the contribution from the phase force, and if we set $f_\alpha^{(n)}(t)=0$, Eq. (3.8) simply expresses a linear response of the real force $F_\alpha^{(n)}(t)$. By definition, we have $\langle \bar{r}_t \rangle_\alpha^{(n)} = \langle \bar{q}_t(t) \rangle_\alpha^{(n)}$.

We next consider a density matrix with a momentum ket interaction, i.e.,

$$\begin{aligned} \sigma'^{(n)}_\alpha(x,r,t) & \equiv \mathrm{Tr}_B[\eta(p_\alpha^{(n)}(\tau))\rho_g] \\ & \equiv \mathrm{Tr}_B[G_\alpha^{(n)}(t,\tau)\eta(\hat{p})G_\alpha^{(n)}(\tau,0)\rho_g] \ . \end{aligned} \tag{3.9}$$

In the path-integral formalism, this is expressed as

$$\begin{aligned} \sigma'^{(n)}_\alpha(x_f,r_f,t) = & \int dx_i \int dr_i \int_{x(0)=x_i}^{x(t)=x_f} D[x] \int_{r(0)=r_i}^{r(t)=r_f} D[r] \exp\left[\frac{i}{\hbar}\Sigma_t[x,r,t;x_i,r_i,\tau]\right] \eta[\partial/\partial r(\tau) + 2\partial/\partial x(\tau)] \\ & \times \exp\left[\frac{i}{\hbar}\Sigma_t[x,r,\tau;x_i,r_i,0] - \frac{1}{\hbar}\Sigma_\beta(x_i,r_i)\right] \ . \end{aligned} \tag{3.10}$$

Since the momentum operator reduces to $M[\dot{r}(\tau)+\dot{x}(\tau)/2]$, we may rewrite

$$\frac{\partial}{\partial r(\tau)} + 2\frac{\partial}{\partial x(\tau)} = \left[\frac{\partial}{\partial b}\exp\left[-bM\int_0^t ds\, \dot{\delta}(s-\tau) r(s) - \frac{bM}{2}\int_0^t ds\, \dot{\delta}(s-\tau) x(s)\right]\right]\Bigg|_{b=0} \ , \tag{3.11}$$

where we performed the partial integration. Thus, the generating function of the density matrix Eq. (3.10) can be obtained from Eq. (2.28) by replacing

$$F_\alpha^{(n)}(t) \to F_\alpha^{(n)}(t) + \frac{ibM\hbar}{2}\dot{\delta}(t-\tau) \ , \quad f_\alpha^{(n)}(t) \to f_\alpha^{(n)}(t) + ibM\hbar\dot{\delta}(t-\tau) \ . \tag{3.12}$$

The result is

$$\sigma'^{(n)}_\alpha(x,r,t) = \left[\eta\left[\frac{\partial}{\partial b}\right]\Xi'^{(n)}_\alpha(x,r,t,b)\right]\Bigg|_{b=0} \ , \tag{3.13}$$

where

$$\begin{aligned} \Xi'^{(n)}_\alpha(x,r,t,b) = & \left[\frac{1}{2\pi\langle q^2\rangle_g}\right]^{1/2} \exp\left[\frac{1}{2\langle q^2\rangle_g}[r - \langle \bar{r}_t\rangle_\alpha^{(n)} - bM\dot{C}(t-\tau)]^2 - \frac{1}{2\hbar}\langle p^2\rangle_g x^2 \right. \\ & \left. + \frac{1}{\hbar}[\langle \bar{p}_t\rangle_\alpha^{(n)} + bM^2\ddot{C}(t-\tau)]x + Q_\alpha^{(n)}(t) + b\langle \bar{p}_t(\tau)\rangle_\alpha^{(n)} + \frac{b^2}{2}M^2\ddot{C}(0)\right] \ , \end{aligned} \tag{3.14}$$

with

$$\begin{aligned} \langle \bar{p}_t(\tau) \rangle_\alpha^{(n)} = & M\int_0^\tau \dot{\chi}(\tau - t') F_\alpha^{(n)}(t') dt' \\ & -\frac{M}{2}\int_\tau^t dt' \dot{\chi}(\tau - t') f_\alpha^{(n)}(t') \\ & + \frac{iM}{\hbar}\int_0^t dt' \dot{S}(\tau - t') f_\alpha^{(n)}(t') \ . \end{aligned} \tag{3.15}$$

In the same way we can evaluate the LGF with a coordinate and a momentum bra interactions, which are defined by

$$\begin{aligned} \sigma''^{(n)}_\alpha(x,r,t) & \equiv \mathrm{Tr}_B[\rho_g \mu^*(q'^{(n)}_\alpha(\tau))] \\ & \equiv \mathrm{Tr}_B(G_\alpha^{(n)}(t,\tau)\{[G_\alpha^{(n)}(\tau,0)\rho_g]\mu^*(\hat{q})\}) \ , \\ \sigma'''^{(n)}_\alpha(x,r,t) & \equiv \mathrm{Tr}_B[\rho_g \eta^*(p'^{(n)}_\alpha(\tau))] \\ & \equiv \mathrm{Tr}_B(G_\alpha^{(n)}(t,\tau)\{[G_\alpha^{(n)}(\tau,0)\rho_g]\eta^*(\hat{p})\}) \ , \end{aligned} \tag{3.16}$$

respectively. We may calculate these LGF's by simply changing the signs of the second terms of $F_\alpha^{(n)}(t)$ in Eqs. (3.4) and (3.12). The results are obtained by replacing the functions $C(t)$, $\langle \bar{q}_t(\tau)\rangle_\alpha^{(n)}$, and $\langle \bar{p}_t(\tau)\rangle_\alpha^{(n)}$ in Eqs. (3.6) and (3.14) by

$$C^*(t) \equiv S(t) + \frac{i\hbar}{2}\chi(t) = \langle q q(t) \rangle_g \ , \tag{3.17}$$

$$\begin{aligned} \langle \bar{q}'_t(\tau) \rangle_\alpha^{(n)} = & \int_0^\tau \chi(\tau - t') F_\alpha^{(n)}(t') dt' \\ & +\tfrac{1}{2}\int_\tau^t dt' \chi(\tau - t') f_\alpha^{(n)}(t') \\ & + \frac{i}{\hbar}\int_0^t dt' S(\tau - t') f_\alpha^{(n)}(t') \ , \end{aligned} \tag{3.18}$$

and

$$\langle \bar{p}_t'(\tau)\rangle_\alpha^{(n)} = \int_0^\tau \dot{\chi}(\tau-t')F_\alpha^{(n)}(t')dt' + \frac{1}{2}\int_\tau^t dt'\dot{\chi}(\tau-t')f_\alpha^{(n)}(t') + \frac{i}{\hbar}\int_0^t dt'\dot{S}(\tau-t')f_\alpha^{(n)}(t') , \quad (3.19)$$

respectively.

The above results can be easily extended to LGF's with general bra and ket interactions similar to Eq. (3.1). The generating functions for this can be obtained from Eq. (2.28) by replacing

$$F_\alpha^{(n)}(t) \to F_\alpha^{(n)}(t) + h_x(t,\{a,b\}) , \quad f_\alpha^{(n)}(t) \to f_\alpha^{(n)}(t) + h_r(t,\{a,b\}) , \quad (3.20)$$

where

$$h_x(t,\{a,b\}) = -\frac{i\hbar}{2}\left[\sum_l a_l\delta(t-\tau_l) - \sum_l a_{l'}'\delta(t-\tau_{l'}) - M\sum_m b_m\dot{\delta}(t-\tau_m) + M\sum_{m'} b_{m'}'\dot{\delta}(t-\tau_{m'})\right] ,$$
$$h_r(t,\{a,b\}) = -i\hbar\left[\sum_l a_l\delta(t-\tau_l) + \sum_l a_{l'}'\delta(t-\tau_{l'}) - M\sum_l b_l\dot{\delta}(t-\tau_l) - M\sum_{l'} b_{l'}'\dot{\delta}(t-\tau_{l'})\right] . \quad (3.21)$$

Here $\{a,b\}$ represents a set of parameters $\{\ldots,a_l,\ldots,a_{l'}',\ldots,b_m,\ldots,b_{m'}'\ldots\}$. Then, from Eqs. (2.33)–(2.35), we have

$$\Xi_\alpha^{(n)}(x,r,t,\{a,b\}) = \left[\frac{1}{2\pi\langle q^2\rangle_g}\right]^{1/2} \exp\left[\frac{1}{2\langle q^2\rangle_g}[r-\langle \bar{r}_t\rangle_\alpha^{(n)} - r_\alpha^{(n)}(t,\{a,b\})]^2 - \frac{1}{2\hbar}\langle p^2\rangle_g x^2 + \frac{1}{\hbar}[\langle \bar{p}_t\rangle_\alpha^{(n)} + p_\alpha^{(n)}(t,\{a,b\})]x + Q_\alpha^{(n)}(t) + X_\alpha^{(n)}(t,\{a,b\})\right] , \quad (3.22)$$

where $\langle \bar{r}_t\rangle_\alpha^{(n)}$ and $\langle \bar{p}_t\rangle_\alpha^{(n)}$ are given in Eqs. (2.33) and (2.34), respectively, and

$$r_\alpha^{(n)}(t,\{a,b\}) = \sum_l a_l C(t-\tau_l) + \sum_l a_{l'}'C^*(t-\tau_{l'}) + M\sum_m b_m\dot{C}(t-\tau_m) + M\sum_{m'} b_{m'}'\dot{C}^*(t-\tau_{m'}) , \quad (3.23)$$

$$p_\alpha^{(n)}(t,\{a,b\}) = M\left[\sum_l a_l\dot{C}(t-\tau_l) + \sum_l a_{l'}'\dot{C}^*(t-\tau_{l'}) + M\sum_m b_m\ddot{C}(t-\tau_m) + M\sum_{m'} b_{m'}'\ddot{C}^*(t-\tau_{m'})\right] , \quad (3.24)$$

and

$$X_\alpha^{(n)}(t,\{a,b\}) = \frac{i}{\hbar}\int_0^t dt'\int_0^{t'} dt''\chi(t'-t'')h_r(t',\{a,b\})[F_\alpha^{(n)}(t'') + h_x(t'',\{a,b\})] + \frac{i}{\hbar}\int_0^t dt'\int_0^{t'} dt''\chi(t'-t'')f_\alpha^{(n)}(t')h_x(t'',\{a,b\}) - \frac{2}{\hbar^2}\int_0^t dt'\int_0^t dt'' S(t'-t'')[2f_\alpha^{(n)}(t') + h_r(t',\{a,b\})]h_r(t'',\{a,b\}) . \quad (3.25)$$

By using these generating functions, the density matrices Eq. (3.1) are expressed as

$$\sigma_\alpha^{(n)}(x,r,t) = [\cdots \eta^*(\partial/\partial b_{l'}')\mu^*(\partial/\partial a_{m'}')\cdots \mu(\partial/\partial a_m)\eta(\partial/\partial b_l)\cdots]\Xi_\alpha^{(n)}(x,r,t,\{a,b\})|_{\{a,b\}=0} . \quad (3.26)$$

Equation (3.26) allows us to evaluate the LGF's $\rho_\alpha^{(n)}(x,r,t)$ [Eq. (2.8)] with interactions $V(p,q)=\mu(q)\eta(p)$ to any order by specializing to a specific choice of the interactions. In Sec. IV we calculate the density matrix with the interaction $V(p,q)=\mu(q)$ to second and fourth orders in H_I.

B. Correlation functions

Experimental observables can usually be expressed in terms of multiple-time correlation functions of the coordinates and momenta. Equation (3.26) also allows us to calculate arbitrary multitime correlation functions.

Consider a coordinate and a momentum expectation value of a ket defined by

$$\langle q_t(\tau)\rangle_\alpha^{(n)} \equiv \mathrm{Tr}[G_\alpha^{(n)}(t,\tau)\hat{q}G_\alpha^{(n)}(\tau,0)\rho_g] , \quad \langle p_t(\tau)\rangle_\alpha^{(n)} \equiv \mathrm{Tr}[G_\alpha^{(n)}(t,\tau)\hat{p}G_\alpha^{(n)}(\tau,0)\rho_g] . \quad (3.27)$$

Since these quantities are defined by acting with q during the process at time τ, $(0<\tau<t)$, they involve two propagation periods and cannot be evaluated from Eq. (2.28). However, they may be evaluated using Eqs. (3.5) and (3.13) by setting $x=0$, and integrating over r. We then have

$$\langle q_t(\tau)\rangle_\alpha^{(n)} = \langle \bar{q}_t(\tau)\rangle_\alpha^{(n)}\exp[Q_\alpha^{(n)}(t)] , \quad \langle p_t(\tau)\rangle_\alpha^{(n)} = \langle \bar{p}_t(\tau)\rangle_\alpha^{(n)}\exp[Q_\alpha^{(n)}(t)] , \quad (3.28)$$

where

$$\langle \bar{q}_t(\tau)\rangle_\alpha^{(n)} = \langle q_t(\tau)\rangle_\alpha^{(n)}/\mathrm{Tr}[\rho_\alpha^{(n)}(t)]\ ,$$
$$\langle \bar{p}_t(\tau)\rangle_\alpha^{(n)} = \langle p_t(\tau)\rangle_\alpha^{(n)}/\mathrm{Tr}[\rho_\alpha^{(n)}(t)]\ , \quad (3.29)$$

and are given by Eqs. (3.8) and (3.15), respectively, and the phase function $Q_\alpha^{(n)}(t)$ is defined by Eq. (2.35). Note that we defined $\langle q_t(\tau)\rangle_\alpha^{(n)}$ and $\langle p_t(\tau)\rangle_\alpha^{(n)}$ for any time $0<\tau<t$; these results also hold for $\tau=t$ or $\tau=0$.

In the same way we can calculate a coordinate and a momentum expectation value of the bra as

$$\langle q_t'(\tau)\rangle_\alpha^{(n)} = \langle \bar{q}_t'(\tau)\rangle_\alpha^{(n)}\exp[Q_\alpha^{(n)}(t)]\ ,$$
$$\langle p_t'(\tau)\rangle_\alpha^{(n)} = \langle \bar{p}_t'(\tau)\rangle_\alpha^{(n)}\exp[Q_\alpha^{(n)}(t)]\ , \quad (3.30)$$

where $\langle \bar{q}_t'(\tau)\rangle_\alpha^{(n)}$ and $\langle \bar{p}_t'(\tau)\rangle_\alpha^{(n)}$ are given by Eqs. (3.18) and (3.19), respectively, and q' and p' refer to the coordinate and the momentum acting on the density matrix bra.

Two-time correlation functions such as

$$\langle q(t)q\rangle_\alpha^{(n)} \equiv \mathrm{Tr}[\hat{q}G_\alpha^{(n)}(t,0)\hat{q}\rho_g]\ ,$$
$$\langle q'q'(t)\rangle_\alpha^{(n)} \equiv \mathrm{Tr}[\hat{q}G_\alpha^{(n)}(t,0)(\rho_g\hat{q})]\ , \quad (3.31)$$

etc., can be similarly evaluated from Eq. (3.22):

$$\langle q(t)q\rangle_\alpha^{(n)} = [C(t)+\langle \bar{q}_t(t)\rangle_\alpha^{(n)}\langle \bar{q}_t(0)\rangle_\alpha^{(n)}]\exp[Q_\alpha^{(n)}(t)]\ , \quad (3.32)$$

$$\langle p(t)q\rangle_\alpha^{(n)} = [M\dot{C}(t)+\langle \bar{p}_t(t)\rangle_\alpha^{(n)}\langle \bar{q}_t(0)\rangle_\alpha^{(n)}]\times\exp[Q_\alpha^{(n)}(t)]\ , \quad (3.33)$$

$$\langle q(t)p\rangle_\alpha^{(n)} = [-M\dot{C}(t)+\langle \bar{q}_t(t)\rangle_\alpha^{(n)}\langle \bar{p}_t(0)\rangle_\alpha^{(n)}]\times\exp[Q_\alpha^{(n)}(t)]\ , \quad (3.34)$$

$$\langle p(t)p\rangle_\alpha^{(n)} = [-M^2\ddot{C}(t)+\langle \bar{p}_t(t)\rangle_\alpha^{(n)}\langle \bar{p}_t(0)\rangle_\alpha^{(n)}]\times\exp[Q_\alpha^{(n)}(t)]\ , \quad (3.35)$$

and

$$\langle q'q'(t)\rangle_\alpha^{(n)} = \langle qq(t)\rangle_\alpha^{(n)} = [C^*(t)+\langle \bar{q}_t'(t)\rangle_\alpha^{(n)}\langle \bar{q}_t'(0)\rangle_\alpha^{(n)}]\exp[Q_\alpha^{(n)}(t)]\ , \quad (3.36)$$

etc., where $C(t)$ and $C^*(t)$ are the coordinate ground correlation functions given by Eqs. (3.7) and (3.17). The functions $\langle \bar{q}_t(t)\rangle_\alpha^{(n)}$, $\langle \bar{q}_t'(t)\rangle_\alpha^{(n)}$, $\langle \bar{p}_t'(t)\rangle_\alpha^{(n)}$, etc. are the prefactors of the position and the momentum expectation values of the bra and the ket and are given by Eqs. (3.8), (3.15), (3.18), and (3.19). If we set these terms, as well as $Q_\alpha^{(n)}(t)$, to zero, the above expressions reduce to the results of the ordinary harmonic oscillator [3].

IV. DYNAMICS OF ELECTRONIC POPULATIONS

By introducing the virtual forces Eq. (2.24), we were able to recast our results in a compact and general form without alluding to a particular order (n) or Liouville-space path α. Here, we present explicit expressions for the LGF for a position-dependent interaction $V(p,q)=\mu(q)$. We start with Eq. (2.5) recast in the form

$$\rho(x,r,t)=\sum_{n=0}^{\infty}\hat{\rho}^{(n)}(x,r,t)\ . \quad (4.1)$$

We shall be interested in electronic populations (as opposed to coherences) and therefore consider even order terms of the expansion, i.e.,

$$\hat{\rho}^{(2)}(x,r,t)=\left[-\frac{i}{\hbar}\right]^2\int_{-\infty}^{t}d\tau_2\int_{-\infty}^{\tau_2}d\tau_1 E(\tau_2)E(\tau_1)\sum_{\alpha=1}^{4}\rho_\alpha^{(2)}(x,r,t)\ , \quad (4.2)$$

$$\hat{\rho}^{(4)}(x,r,t)=\left[-\frac{i}{\hbar}\right]^4\int_{-\infty}^{t}d\tau_4\int_{-\infty}^{\tau_3}d\tau_3\int_{-\infty}^{\tau_3}d\tau_2\int_{-\infty}^{\tau_2}d\tau_1 E(\tau_4)E(\tau_3)E(\tau_2)E(\tau_1)\sum_{\alpha=1}^{16}\rho_\alpha^{(4)}(x,r,t)\ , \quad (4.3)$$

and

$$\hat{\rho}^{(2N)}(x,r,t)=\left[-\frac{i}{\hbar}\right]^{2N}\left[\prod_{k=1}^{2N}\int_{-\infty}^{\tau_{k+1}}d\tau_k\right]\left[\prod_{k=1}^{2N}E(\tau_k)\right]\sum_{\alpha=1}^{2^N}\hat{\rho}_\alpha^{(2N)}(x,r,t)\ , \quad (4.4)$$

where

$$\hat{\rho}_\alpha^{(2N)}(x,r,t)=\left[\frac{1}{2\pi\langle q^2\rangle_g}\right]^{1/2}\times\left\{\left[\prod_{k=1}^{2N}\mu\left[\frac{\partial}{\partial c_k}\right]\right]\exp\left[\frac{1}{2\langle q^2\rangle_g}[r-\langle \bar{r}_t\rangle_\alpha^{(2N)}-r_\alpha^{(2N)}(t,\{c\})]^2-\frac{1}{2\hbar}\langle p^2\rangle_g x^2+\frac{1}{\hbar}[\langle \bar{p}_t\rangle_\alpha^{(2N)}+p_\alpha^{(2N)}(t,\{c\})]x+Q_\alpha^{(2N)}(t)+X_\alpha^{(2N)}(t,\{c\})\right]\right\}\Bigg|_{c_k=0}\ , \quad (4.5)$$

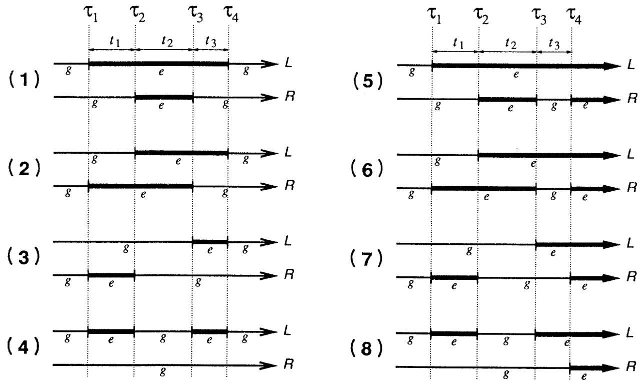

FIG. 3. Doubled-sided Feynman diagrams in fourth order. The paths 1–4 correspond to the process g to g, whereas 5–8 correspond to g to e. The Hermitian conjugate paths of 1–8, which can be obtained by interchanging L and R, respectively, are not shown here.

TABLE III. Auxiliary parameters to calculate LGF to fourth order.

α	ϵ_1	ϵ_2	ϵ_3	ϵ_4
1	+	+	+	−
2	−	+	+	−
3	−	−	+	−
4	+	−	+	−

and α indicates the Liouville paths such as the ones given in Figs. 2 and 3 and their complex conjugate. To write the result in compact form, it is convenient to introduce sign parameters $\epsilon_i = \pm$ for a time period $\tau_j < t < \tau_{j+1}$ [18]. We chose $\epsilon_{2j-1} = +\ (-)$ for the eg (ge) state for an odd time period where a density matrix is in a coherence. We further chose $\epsilon_{2j} = +(-)$ for the ee (gg) state for an even time period where a density matrix is in a population. As an example, parameters of the fourth-order terms corresponding to $\alpha = 1$–4 in Fig. 3 are shown in Table III. Functions in Eq. (2.24) are then expressed as

$$F_\alpha^{(2N)}(s) = -\frac{\hbar\xi}{2}\left[1+\sum_{j=1}^{N}\epsilon_{2j}[\Theta(s-\tau_{2j})-\Theta(s-\tau_{2j+1})]\right],$$

$$f_\alpha^{(2N)}(s) = -\hbar\xi\sum_{j=1}^{N}\epsilon_{2j-1}[\Theta(s-\tau_{2j-1})-\Theta(s-\tau_{2j})],$$

$$\Phi_\alpha^{(2N)}(s) = -\hbar(\omega_{eg}+\lambda)\sum_{j=1}^{N}\epsilon_{2j-1}[\Theta(s-\tau_{2j-1})-\Theta(s-\tau_{2j})], \tag{4.6}$$

where $\Theta(t)$ is the step function and α now refers to the set $\{\epsilon_j\} = \{\epsilon_1, \epsilon_2, \ldots, \epsilon_{2N}\}$ and

$$\lambda \equiv \frac{MD^2\omega_0^2}{2\hbar}, \quad \xi \equiv \frac{MD\omega_0^2}{\hbar}. \tag{4.7}$$

Inserting the above functions into Eqs. (2.33)–(2.35), we can calculate the coordinate, momentum, and phase functions in Eq. (4.5) as

$$\langle \bar{r}_t \rangle_\alpha^{(2N)} = -i\xi^{-1}\left[\sum_{j=0}^{N-1}\epsilon_{2j+1}\dot{g}_{\epsilon_{2j}\epsilon_{2j+1}}(t-\tau_{2j+1}) - \sum_{j=1}^{N}\epsilon_{2j-1}\dot{g}_{\epsilon_{2j}\epsilon_{2j-1}}(t-\tau_{2j})\right], \tag{4.8}$$

$$\langle \bar{p}_t \rangle_\alpha^{(2N)} = -iM\xi^{-1}\left[\sum_{j=0}^{N-1}\epsilon_{2j+1}\ddot{g}_{\epsilon_{2j}\epsilon_{2j+1}}(t-\tau_{2j+1}) - \sum_{j=1}^{N}\epsilon_{2j-1}\ddot{g}_{\epsilon_{2j}\epsilon_{2j-1}}(t-\tau_{2j})\right], \tag{4.9}$$

and

$$\begin{aligned} Q_\alpha^{(2N)}(t) = & -i(\omega_{eg}+\lambda)\sum_{j=1}^{N}\epsilon_{2j-1}(\tau_{2j}-\tau_{2j-1}) - \sum_{j=1}^{N} g_{\epsilon_{2j-1}\epsilon_{2j-2}}(\tau_{2j}-\tau_{2j-1}) \\ & - \sum_{j=k+1}^{N}\sum_{k=1}^{N-1}\epsilon_{2j-1}\epsilon_{2k-1}[\dot{g}_{\epsilon_{2k}\epsilon_{2k-1}}(\tau_{2j-1}-\tau_{2k}) - \dot{g}_{\epsilon_{2k}\epsilon_{2k-1}}(\tau_{2j}-\tau_{2k}) \\ & - \dot{g}_{\epsilon_{2k-1}\epsilon_{2k-2}}(\tau_{2j-1}-\tau_{2k-1}) + \dot{g}_{\epsilon_{2k-1}\epsilon_{2k-2}}(\tau_{2j}-\tau_{2k-1})], \end{aligned} \tag{4.10}$$

where $\epsilon_0 = -$ and we introduced the auxiliary functions which create the line-shape function defined by (see Appendix C)

$$g_\pm(t) \equiv \xi^2\int_0^t dt'\int_0^{t'} dt''\left[S(t'') \pm \frac{i\hbar}{2}\chi(t'')\right]. \tag{4.11}$$

Using ϵ_j, we can express the generating forces, Eq. (3.21), in the form

$$h_x(t,\{c\}) = \frac{i\hbar}{2}\sum_{k=1}^{2N}\epsilon_{k-1}\epsilon_k c_k\delta(t-\tau_k),$$

$$h_r(t,\{c\}) = -i\hbar\sum_{k=1}^{2N} c_k\delta(t-\tau_k). \tag{4.12}$$

Then the generating coordinate, momentum, and phase functions defined by Eqs. (3.23)–(3.25) can be evaluated as

$$r_\alpha^{(2N)}(t,\{c\})=\xi^{-2}\sum_{k=1}^{2N} c_k\ddot{g}_{\epsilon_k\epsilon_{k-1}}(t-\tau_k)\ , \tag{4.13}$$

$$p_\alpha^{(2N)}(t,\{c\})=M\xi^{-2}\sum_{k=1}^{2N} c_k\dddot{g}_{\epsilon_k\epsilon_{k-1}}(t-\tau_k)\ , \tag{4.14}$$

and

$$X_\alpha^{(2N)}(t)=\sum_{k=1}^{2N} c_k\langle\bar{q}_k(\{\tau\})\rangle_\alpha^{(2N)}+\xi^{-2}\sum_{k=m+1}^{2N}\sum_{m=1}^{2N-1} c_k c_m\ddot{g}_{\epsilon_m\epsilon_{m-1}}(\tau_k-\tau_m)+\xi^{-2}\sum_{k=1}^{2N}\frac{c_k^2}{2}\ddot{g}(0)\ , \tag{4.15}$$

with

$$\langle\bar{q}_k(\{\tau\})\rangle_\alpha^{(2N)}=-i\xi^{-1}\left[\sum_{m=0}^{k>2m+1}\epsilon_{2m+1}\dot{g}_{\epsilon_{2m}\epsilon_{2m+1}}(\tau_k-\tau_{2m+1})-\sum_{m=1}^{k>2m}\epsilon_{2m-1}\dot{g}_{\epsilon_{2m}\epsilon_{2m-1}}(\tau_k-\tau_{2m})-\sum_{2m+1>k}^{m=N-1}\epsilon_{2m+1}\dot{g}_{\epsilon_k\epsilon_{k-1}}(\tau_{2m+1}-\tau_k)+\sum_{2m>k}^{m=N}\epsilon_{2m-1}\dot{g}_{\epsilon_k\epsilon_{k-1}}(\tau_{2m}-\tau_k)\right]\ . \tag{4.16}$$

The above result allows us to study dynamics of electronic distribution functions in the displaced harmonic potential coupled by the interaction $\mu(q)$. In the next section, we apply these results to calculation of the nonlinear-optical response in condensed phases.

V. NONLINEAR-OPTICAL RESPONSE WITH NON-CONDON INTERACTIONS

The results of the previous section can also be applied to study the nonlinear-optical response by substituting $V(p,q)\equiv\mu(q)$ as a non-Condon dipole moment and taking $E(t)$ to be the external electric field. The optical response can be expressed in terms of the optical polarization

$$P(\mathbf{r},t)\equiv \mathrm{Tr}[\mu(q)(|e\rangle\langle g|+|g\rangle\langle e|)\rho(t)]\ , \tag{5.1}$$

in which $\rho(t)$ involves the interaction between the driving field and the system. If the interaction between the system and the electric field is weak, we may expand $\rho(t)$ and consequently $P(\mathbf{r},t)$ in powers of the electric field. For our model, the second-order polarization vanishes, so that the lowest nonlinear contribution is third order. We thus have

$$P(\mathbf{r},t)=\sum_{N=1}^{\infty}P^{(2N-1)}(\mathbf{r},t)\ , \tag{5.2}$$

where

$$P^{(1)}(\mathbf{r},t)=-\frac{i}{\hbar}\int_0^\infty dt_1 E(\mathbf{r},t-t_1)R_1^{(1)}(t_1)+\text{c.c.}\ , \tag{5.3}$$

$$P^{(3)}(\mathbf{r},t)=\frac{i}{\hbar^3}\int_0^\infty dt_3\int_0^\infty dt_2\int_0^\infty dt_1 E(\mathbf{r},t-t_3)\times E(\mathbf{r},t-t_2-t_3)E(\mathbf{r},t-t_1-t_2-t_3)\times\sum_{\alpha=1}^{4}R_\alpha^{(3)}(t_3,t_2,t_1)+\text{c.c.}\ , \tag{5.4}$$

and

$$P^{(2N-1)}(\mathbf{r},t)=\left[-\frac{i}{\hbar}\right]^{2N-1}\left[\prod_{k=1}^{2N-1}\int_0^\infty dt_k\right]\times\left[\prod_{k=1}^{2N-1}E(\mathbf{r},t-\sum_{m=1}^{k}t_m)\right]\times\sum_{\alpha=1}^{2^N}R_\alpha^{(2N-1)}(\{t_k\})+\text{c.c.}\ , \tag{5.5}$$

where we introduced the time variable $t_k=\tau_{k+1}-\tau_k$, and $R_\alpha^{(2N-1)}(\{t_k\})$ are the $(2N-1)$th-order response functions for the specific Liouville path α. As examples, here we write down the first- and third-order polarizations as

$$R_1^{(1)}(t_1)=\langle\mu(q(\tau))\mu(q(\tau-t_1))\rangle_1^{(2)}\ , \tag{5.6}$$

and

$$\begin{aligned}
R_1^{(3)}(t_3,t_2,t_1)&=\langle\mu(q(\tau))\mu(q(\tau-t_1-t_2-t_3))\mu(q'(\tau-t_2-t_3))\mu(q'(\tau-t_3))\rangle_1^{(4)}\ ,\\
R_2^{(3)}(t_3,t_2,t_1)&=\langle\mu(q(\tau))\mu(q(\tau-t_2-t_3))\mu(q'(\tau-t_1-t_2-t_3))\mu(q'(\tau-t_3))\rangle_2^{(4)}\ ,\\
R_3^{(3)}(t_3,t_2,t_1)&=\langle\mu(q(\tau))\mu(q(\tau-t_3))\mu(q'(\tau-t_1-t_2-t_3))\mu(q'(\tau-t_2-t_3))\rangle_3^{(4)}\ ,\\
R_4^{(3)}(t_3,t_2,t_1)&=\langle\mu(q(\tau))\mu(q(\tau-t_3))\mu(q(\tau-t_2-t_3))\mu(q(\tau-t_1-t_2-t_3))\rangle_4^{(4)}\ ,
\end{aligned} \tag{5.7}$$

where subscripts refer to the Liouville paths given in Figs. 2 and 3.

By integrating the generating function Eq. (4.5) over x and r, we have the $(2N-1)$th-order response functions in the form

$$R_{\alpha}^{(2N-1)}(\{t\})=\left[\left[\prod_{k=1}^{2N}\mu(\partial/\partial c_k)\right]\exp[Q_{\alpha}^{(2N)}(\{t\})+X_{\alpha}^{(2N)}(\{t\};\{c\})]\right]\Bigg|_{\{c\}=0}, \tag{5.8}$$

where

$$\begin{aligned}Q_{\alpha}^{(2N)}(\{t\})=&-i\omega'_{eg}\sum_{j=1}^{N}\epsilon_{2j-1}t_{2j-1}-\sum_{j=1}^{N}g_{\epsilon_{2j-1}\epsilon_{2j-2}}(t_{2j-1})\\&-\sum_{j=k+1}^{N}\sum_{k=1}^{N-1}\epsilon_{2j-1}\epsilon_{2k-1}\left[\dot g_{\epsilon_{2k}\epsilon_{2k-1}}\left[\sum_{l=2k}^{2j-2}t_l\right]-\dot g_{\epsilon_{2k}\epsilon_{2k-1}}\left[\sum_{l=2k}^{2j-1}t_l\right]\right.\\&\left.-\dot g_{\epsilon_{2k-1}\epsilon_{2k-2}}\left[\sum_{l=2k-1}^{2j-2}t_l\right]+\dot g_{\epsilon_{2k-1}\epsilon_{2k-2}}\left[\sum_{l=2k-1}^{2j-1}t_l\right]\right]\end{aligned} \tag{5.9}$$

and

$$X_{\alpha}^{(2N)}(\{t\})=\sum_{k=1}^{2N}c_k\langle\bar q_k(\{t\})\rangle_{\alpha}^{(2N)}+\xi^{-2}\sum_{k=m+1}^{2N}\sum_{m=1}^{2N-1}c_kc_m\ddot g_{\epsilon_m\epsilon_{m-1}}\left[\sum_{l=k}^{m-1}t_l\right]+\xi^{-2}\sum_{k=1}^{2N}\frac{c_k^2}{2}\ddot g(0), \tag{5.10}$$

with

$$\begin{aligned}\langle\bar q_k(\{t\})\rangle_{\alpha}^{(2N)}=-i\xi^{-1}&\left[\sum_{m=0}^{k>2m+1}\epsilon_{2m+1}\dot g_{\epsilon_{2m}\epsilon_{2m+1}}\left[\sum_{l=2m+1}^{k-1}t_l\right]-\sum_{m=1}^{k>2m}\epsilon_{2m-1}\dot g_{\epsilon_{2m}\epsilon_{2m-1}}\left[\sum_{l=2m}^{k-1}t_l\right]\right.\\&\left.-\sum_{2m+1>k}^{m=N-1}\epsilon_{2m+1}\dot g_{\epsilon_k\epsilon_{k-1}}\left[\sum_{l=k}^{2m}t_l\right]+\sum_{2m>k}^{m=N}\epsilon_{2m-1}\dot g_{\epsilon_k\epsilon_{k-1}}\left[\sum_{l=k}^{2m-1}t_l\right]\right].\end{aligned} \tag{5.11}$$

In the above, the label α refers to a set of sign parameters $\{\epsilon\}=\{\epsilon_1,\epsilon_2,\ldots,\epsilon_{2N-1}\}$ and $\omega'_{eg}\equiv\omega_{eg}+\lambda$. The second- and the fourth-order response function are then expressed as

$$R_1^{(1)}(t_1)=\{\mu(\partial/\partial c_2)\mu(\partial/\partial c_1)\exp[Q_1^{(2)}(t_1)+X_1^{(2)}(t_1,\{c\})]\}|_{\{c\}=0}, \tag{5.12}$$

and

$$\begin{aligned}R_1^{(3)}(t_3,t_2,t_1)&=(\mu(\partial/\partial c_4)\mu(\partial/\partial c_3)\mu(\partial/\partial c_2)\mu(\partial/\partial c_1)\exp[Q_{+++}^{(4)}(\{t\})+X_{+++}^{(4)}(\{t\};\{c\})])|_{\{c\}=0},\\R_2^{(3)}(t_3,t_2,t_1)&=(\mu(\partial/\partial c_4)\mu(\partial/\partial c_3)\mu(\partial/\partial c_2)\mu(\partial/\partial c_1)\exp[Q_{-++}^{(4)}(\{t\})+X_{-++}^{(4)}(\{t\};\{c\})])|_{\{c\}=0},\\R_3^{(3)}(t_3,t_2,t_1)&=(\mu(\partial/\partial c_4)\mu(\partial/\partial c_3)\mu(\partial/\partial c_2)\mu(\partial/\partial c_1)\exp[Q_{--+}^{(4)}(\{t\})+X_{--+}^{(4)}(\{t\};\{c\})])|_{\{c\}=0},\\R_4^{(3)}(t_3,t_2,t_1)&=(\mu(\partial/\partial_4)\mu(\partial/\partial c_3)\mu(\partial/\partial_2)\mu(\partial/\partial c_1)\exp[Q_{+-+}^{(4)}(\{t\})+X_{+-+}^{(4)}(\{t\};\{c\})])|_{\{c\}=0},\end{aligned} \tag{5.13}$$

where

$$Q_1^{(2)}(t_1)=-i\omega'_{eg}t_1-g_-(t_1), \tag{5.14}$$

$$X_1^{(2)}(t_1,\{c\})=-i\xi^{-1}\dot g_-(t_1)(c_1+c_2)+\xi^{-2}[\ddot g_-(t_1)c_1c_2+\tfrac{1}{2}(c_1^2+c_2^2)\ddot g(0)], \tag{5.15}$$

$$\begin{aligned}Q_{\epsilon_1\epsilon_2\epsilon_3}^{(4)}(t_3,t_2,t_1)=&-i\omega'_{eg}(\epsilon_1t_1+\epsilon_3t_3)-g_{-\epsilon_1}(t_1)-g_{\epsilon_2\epsilon_3}(t_3)\\&-\epsilon_1\epsilon_3[g_{\epsilon_1\epsilon_2}(t_2)-g_{\epsilon_1\epsilon_2}(t_2+t_3)-g_{-\epsilon_1}(t_1+t_2)+g_{-\epsilon_1}(t_1+t_2+t_3)],\end{aligned} \tag{5.16}$$

$$\begin{aligned}X_{\epsilon_1\epsilon_2\epsilon_3}^{(4)}(t_3,t_2,t_1,\{c\})=&c_1\langle\bar q_1(t_3,t_2,t_1)\rangle_{\epsilon_1\epsilon_2\epsilon_3}^{(4)}+c_2\langle\bar q_2(t_3,t_2,t_1)\rangle_{\epsilon_1\epsilon_2\epsilon_3}^{(4)}+c_3\langle\bar q_3(t_3,t_2,t_1)\rangle_{\epsilon_1\epsilon_2\epsilon_3}^{(4)}+c_4\langle\bar q_4(t_3,t_2,t_1)\rangle_{\epsilon_1\epsilon_2\epsilon_3}^{(4)}\\&+\xi^{-2}[c_1c_2\ddot g_{-\epsilon_1}(t_1)+c_1c_3\ddot g_{-\epsilon_1}(t_1+t_2)+c_2c_3\ddot g_{\epsilon_1\epsilon_2}(t_2)+c_1c_4\ddot g_{-\epsilon_1}(t_1+t_2+t_3)\\&+c_2c_4\ddot g_{\epsilon_1\epsilon_2}(t_2+t_3)+c_3c_4\ddot g_{\epsilon_2\epsilon_3}(t_3)+\tfrac{1}{2}(c_1^2+c_2^2+c_3^2+c_4^2)\ddot g(0)],\end{aligned} \tag{5.17}$$

with

$$\begin{aligned}
\langle \bar{q}_1(t_1,t_2,t_3)\rangle^{(4)}_{\epsilon_1\epsilon_2\epsilon_3} &= -i\xi^{-1}[\epsilon_1\dot{g}_{-\epsilon_1}(t_1)-\epsilon_3\dot{g}_{-\epsilon_1}(t_1+t_2)+\epsilon_3\dot{g}_{-\epsilon_1}(t_1+t_2+t_3)]\ ,\\
\langle \bar{q}_2(t_1,t_2,t_3)\rangle^{(4)}_{\epsilon_1\epsilon_2\epsilon_3} &= -i\xi^{-1}[\epsilon_1\dot{g}_{-\epsilon_1}(t_1)+\epsilon_3\dot{g}_{\epsilon_1\epsilon_2}(t_2+t_3)-\epsilon_3\dot{g}_{\epsilon_1\epsilon_2}(t_2)]\ ,\\
\langle \bar{q}_3(t_1,t_2,t_3)\rangle^{(4)}_{\epsilon_1\epsilon_2\epsilon_3} &= -i\xi^{-1}[\epsilon_1\dot{g}_{-\epsilon_1}(t_1+t_2)-\epsilon_1\dot{g}_{\epsilon_1\epsilon_2}(t_2)+\epsilon_3\dot{g}_{\epsilon_2,\epsilon_3}(t_3)]\ ,\\
\langle \bar{q}_4(t_1,t_2,t_3)\rangle^{(4)}_{\epsilon_1\epsilon_2\epsilon_3} &= -i\xi^{-1}[\epsilon_1\dot{g}_{-\epsilon_1}(t_1+t_2+t_3)-\epsilon_1\dot{g}_{\epsilon_1\epsilon_2}(t_2+t_3)+\epsilon_3\dot{g}_{\epsilon_2\epsilon_3}(t_3)]\ .
\end{aligned} \tag{5.18}$$

Numerous applications to frequency-domain and time-domain ultrafast techniques have been made to Eqs. (5.3) and (5.4) using $R_1^{(1)}(t_1)$ and $R_\alpha^{(3)}(t_3,t_2,t_1)$ with the Condon approximation. The present results provide a generalization to non-Condon interactions and to optical processes of any order. One technique where non-Condon effects are important is impulsive Raman spectroscopy. It has been analyzed in detail for resonant excitation within the Condon approximation [1(c), 20]. For off resonance, the non-Condon contribution is dominant and the signal can be written in terms of a response function of a nuclear coordinate, originating from the coordinate dependence of μ [5]. Our results provide a useful expression which interpolates between these limits.

As a simple application of these results, we have calculated the linear absorption spectrum of a model system which includes a single vibrational mode in a medium. The absorption line shape is given by

$$I(\omega)=\int_0^\infty dt\, R_1^{(1)}(t_1)\exp(i\omega t)+\text{c.c.} \tag{5.19}$$

We have allowed for the variation of the transition dipole with the nuclear coordinate (non-Condon effects) and assumed

$$\mu(q)=\mu_0+\mu_0' q+\tfrac{1}{2}\mu_0'' q^2\ , \tag{5.20}$$

where

$$\mu_0=\mu(0),\quad \mu_0'=\left.\frac{d\mu(q)}{dq}\right|_{q=0},\quad \mu_0''=\left.\frac{d^2\mu(q)}{dq^2}\right|_{q=0}. \tag{5.21}$$

We assume a frequency-independent damping, $\tilde{\gamma}(\omega)=\gamma$, where analytical expressions of symmetrized and antisymmetrized correlation functions are known [3]. The auxiliary function is then given by

$$g_\pm(t)=g'(t)\pm ig''(t)\ , \tag{5.22}$$

where

$$g'(t)=\lambda\left\{\left[\frac{\lambda_1^2}{2\zeta\omega_0^2}(e^{-\lambda_2 t}+\lambda_2 t-1)\coth\left[\frac{i\beta\hbar\lambda_2}{2}\right]-\frac{\lambda_2^2}{2\zeta\omega_0^2}(e^{-\lambda_1 t}+\lambda_1 t-1)\coth\left[\frac{i\beta\hbar\lambda_1}{2}\right]\right]-\frac{4\gamma\omega_0^2}{\beta\hbar}\sum_{n=1}^{\infty}\frac{1}{\nu_n}\frac{e^{-\nu_n t}+\nu_n t-1}{(\omega_0^2+\nu_n^2)^2-\gamma^2\nu_n^2}\right\} \tag{5.23}$$

and

$$ig''(t)=i\lambda\left[e^{-\gamma t/2}\left[\frac{\gamma^2/2-\omega_0^2}{\zeta\omega_0^2}\sin(\zeta t)+\frac{\gamma}{\omega_0^2}\cos(\zeta t)\right]+t-\frac{\gamma}{\omega_0^2}\right]. \tag{5.24}$$

In the above we defined $\nu_n=2\pi n/\hbar\beta$ and

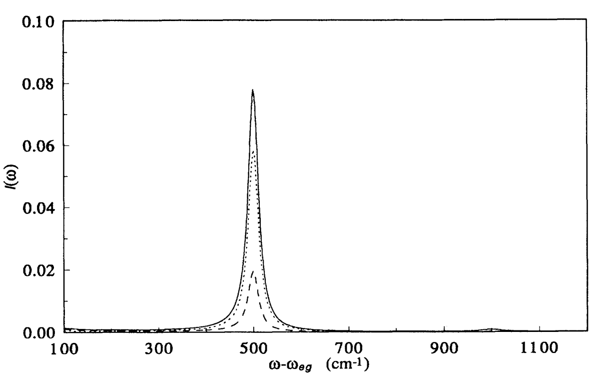

FIG. 4. Absorption spectrum [Eq. (5.19)] with Condon and non-Condon dipole interactions for a weak damping case, $\gamma=0.05\omega_0$. The fundamental 0-0 transition (not shown) is 230 times more intense. The solid line ($\mu'=0.1,\mu''=0.01$) indicates the non-Condon interaction, whereas the dashed line indicates the Condon approximation. The difference between these two lines is shown by the dotted line.

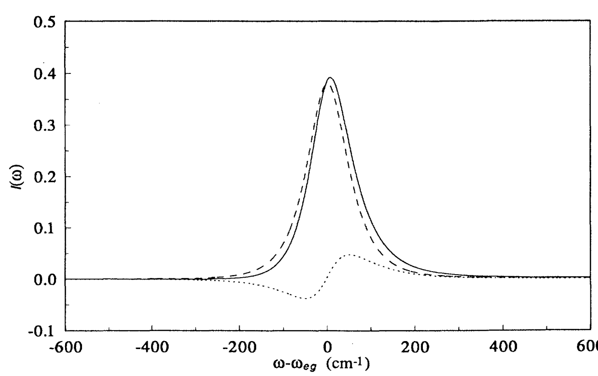

FIG. 5. Absorption spectrum for a strong damping $\gamma=5\omega_0$. Other parameters are the same as in Fig. 4.

$$\lambda_1=\frac{\gamma}{2}+i\zeta,\ \ \lambda_2=\frac{\gamma}{2}-i\zeta,\ \ \zeta=(\omega_0^2-\gamma^2/4)^{1/2}\ . \tag{5.25}$$

Figure 4 compares the absorption spectrum for this model with the spectrum in the Condon approximation ($\mu'=\mu''=0$) for an underdamped mode ($\gamma=0.05\omega_0$) with $\omega_0=500$ cm^{-1}, $D=0.1\sqrt{\hbar/M\omega_0}$, $T=300$ K, $\mu_0'=0.1$, and $\mu_0''=0.01$. This model can represent a high-frequency intramolecular optically active mode or an impurity in a crystal. In the figure we show the vibronic sideband 0-1 transition. The fundamental 0-0 transition (not shown) is 230 times more intense. In Fig. 5 we show the absorption for an overdamped mode $\gamma=5\omega_0$ in the vicinity of the origin. This can represent a solvent coordinate related, e.g., to macroscopic dielectric fluctuations in a polar medium.

VI. APPLICABILITY OF THE SEMICLASSICAL LANGEVIN EQUATION

Because of the correlation between the system and the environment, it is not generally possible to factorize the propagator in the form

$$\exp\left\{\frac{i}{\hbar}\Sigma_t(x_f,r_f,t;x_i,r_i,0)\right\}=\int dx_\tau\int dr_\tau \exp\left\{\frac{i}{\hbar}\Sigma_t(x_f,r_f,t;x_\tau,r_\tau,\tau)\right\}\exp\left\{\frac{i}{\hbar}\Sigma_t(x_\tau,r_\tau,\tau;x_i,r_i,0)\right\}\ . \tag{6.1}$$

Such factorization implies the existence of a *reduced description* whereby the bath degrees of freedom are always in equilibrium and we can follow explicitly just a single degree of freedom x and r. The classical Langevin equation is a common example of a reduced description. When such a level of description applies, we can describe each segment of the Liouville-space path in terms of a conditional probability and an accumulating phase factor [5,20].

In order to find conditions of the factorization Eq. (6.1) to hold, we substituted Eq. (2.27) into both sides of the above equation and compared the terms in the exponent. The following conditions need to be satisfied for Eq. (6.1) to hold:

$$\frac{1}{\hbar\Lambda}S(t)=\dot{\chi}(t)\ , \tag{6.2}$$

$$\chi(t_1+t_2)\propto[\dot{\chi}(t_1)\chi(t_2)+\chi(t_1)\dot{\chi}(t_2)]\ , \tag{6.3}$$

and

$$\dot{\chi}(t)^2-\chi(t)\ddot{\chi}(t)=M^{-2},\ \text{ or }\ \dot{\chi}(t)^2-\chi(t)\ddot{\chi}(t)=0\ , \tag{6.4}$$

where the last condition was found from the x_f^2 factor. As seen from the definition Eqs. (2.30) and (2.31), the first condition can be met provided the temperature of the environment is sufficiently high, i.e., $\coth(\hbar\beta\omega/2)\approx 2/\hbar\beta\omega$. The second and third conditions are satisfied only when

$$\chi(t)=\frac{1}{M\omega}\sin(\omega t) \tag{6.5}$$

or

$$\chi(t)=Ce^{-\alpha t}\ , \tag{6.6}$$

where C and α are the constants. As seen from the definition, Eq. (2.30), Eq. (6.5) corresponds to the simple case of an isolated system with no damping, $\tilde{\gamma}(\omega)=\gamma\ll\omega_0$. Equation (6.6) corresponds to the Ohmic dissipation with strong damping, $\tilde{\gamma}(\omega)=\gamma\gg\omega_0$, so that when the oscillator motion is overdamped, then $C=M/\gamma$ and $\alpha=\omega_0^2/\gamma$. Using the high-temperature condition $2/\hbar\beta\omega_0\ll 1$, we may replace all $S(t)$ and $g_\pm(t)$ in the previous sections by

$$S(t)\rightarrow\frac{1}{M\beta\omega_0^2}M'(t)\ , \tag{6.7}$$

and

$$g_\pm(r)\rightarrow g'_\pm(t)=\pm i\lambda\left[t-\int_0^t dt'M'(t')\right]+\Delta^2\int_0^t dt'\int_0^{t'}dt''M'(t'')\ , \tag{6.8}$$

respectively, where $\Delta^2=2\lambda/\beta\hbar$ and

$$M'(t)\equiv 1-M\omega_0^2\int_0^t dt'\chi(t')=\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\frac{\omega_0^2\tilde{\gamma}(\omega)}{(\omega_0^2-\omega^2)^2+\omega^2\tilde{\gamma}^2(\omega)}\cos(\omega t) \tag{6.9}$$

(see Appendix C).

We are now in a position to define precisely the range of validity of the semiclassical Langevin equation obtained in Ref. [20]. When the following three conditions are met: (i) Ohmic dissipation [$\tilde{\gamma}(\omega)$ independent on ω], (ii) strongly overdamped motion $\gamma\gg\omega_0$, and (iii) high-temperature $\beta\hbar\omega_0\ll 1$, the equation of motion, Eq. (2.25) with Eq. (2.26), reduces to the semiclassical Langevin equation derived by Yan and Mukamel,

$$\ddot{r}+\gamma\dot{r}+\omega_0^2 r-\frac{1}{M}F_\alpha^{(n)}(t)=f(t)\ , \tag{6.10}$$

where the noise $f(t)$ results from Eq. (2.26) and $\langle f(t)f(t')\rangle=\gamma\delta(t-t')/\beta$. The above equation with condition (ii) is equivalent to the Smolchowski equation. Under these conditions, the Wigner function $W_\alpha^{(n)}(p,q,t)$, the response functions $R_\alpha^{(2N-1)}(\{t\})$, etc. agree with our results. When either of these conditions is not satisfied, then the solution of the Langevin equation is in general different from the path-integral result.

VII. CONCLUDING REMARKS

The present results provide an exact expression for the Liouville-space generating function which includes a bath with any temperature, to multitime correlation functions and to include non-Condon effects. The latter are particularly important in, e.g., off-resonant Raman-scattering measurements where the coordinate dependence of the transition dipole proceeds the dominant mechanism [5,27].

In curve-crossing problems, the nonadiabatic coupling is often taken to be localized in the crossing region. Consider a double-well system connected by a nonadiabatic interaction $\mu(q)$. The function $\mu(q)$ is often localized in the crossing regions [9,14,28]. We assume that the rate process is described by a master equation,

$$\frac{dW_g(t)}{dt}=-KW_g(t)+K'W_e(t) . \tag{7.1}$$

Here we denote the population of $|g\rangle$ by $W_g(t)$ and of $|e\rangle$ by $W_e(t)$, and K and K' are the rate constants for the forward (g to e) and reverse (e to g) processes. We shall focus here on the forward rate K. The reverse rate K' can be simply obtained by changing the indices g and e. This rate can be expressed by using the response functions as [12,20]

$$K=K_2-K_4+\cdots , \tag{7.2}$$

where

$$K_2=\frac{1}{\hbar^2}\int_0^\infty dt_1 R_1^{(1)}(t_1)+\text{c.c.} \tag{7.3}$$

and

$$K_4=\frac{1}{\hbar^4}\int_0^\infty dt_3\int_0^\infty dt_2\int_0^\infty dt_1 \sum_{\alpha=1}^{4}(R_\alpha^{(3(}(t_3,t_2,t_1) -R_\alpha^{(3)}(t_3,\infty,t_1))+\text{c.c.} , \tag{7.4}$$

in which $R_1^{(1)}(t_1)$ and $R_\alpha^{(3)}(t_3,t_2,t_1)$ are given by Eqs. (5.12) and (5.13), respectively. By using the results of the previous section for $R_1^{(1)}(t_1)$ and $R_\alpha^{(3)}(t_3,t_2,t_1)$, we have generalized these results to include the coordinate dependence of the nonadiabatic coupling $\mu(q)$.

We also note that the extension to incorporating several system modes is straightforward. The generating function and density matrix is simply the product of the present expressions. This is the basis for the multimode Brownian oscillator model, which was applied successfully to many systems [1(c),5]. Another extension is to include a general anharmonic potential of the system. The Langevin equation

$$\ddot{r}+\gamma\dot{r}-\frac{1}{M}F_\alpha'^{(n)}(r,t)=f(t) , \tag{7.5}$$

with the force defined by the anharmonic potentials U_L and U_R,

$$F_\alpha'^{(n)}(r,s)=-\left[\frac{d}{dx}[U_L(r+x/2,s) -U_R(r-x/2,s)]\right]\Bigg|_{x=0} \tag{7.6}$$

and the noise $f(t)[\langle f(t)f(t')\rangle=\gamma\delta(t-t')/\beta]$ may provide a useful semiclassical approximation in this case.

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APPENDIX A: THE CORRELATED STATE

The correlated state $\rho_g^{\text{cs}}(q,q';q_i,q_i')$ used in Eq. (2.12) is studied in Ref. [3] and is expressed as

$$\rho_g^{\text{cs}}(q,q';q_i,q_i')=\exp\left[-\frac{M}{\hbar}\left[\frac{1}{2\Lambda}\frac{(q_i+q_i')^2}{4}+\frac{\Omega}{2}(q_i-q_i')^2\right]+\frac{iM}{\hbar}\int_0^t ds[q(s)-q'(s)] \times\left[\frac{(q_i+q_i')}{2}C_1(s)-i(q_i-q_i')C_2(s)+\frac{i}{2}\int_0^t du\, R'(s,u)[q(u)-q'(u)]\right]\right] , \tag{A1}$$

where the functions and the constants are expressed in the Fourier transformation form of the Matsubara frequency, $\nu_n=2\pi n/\hbar\beta$, as

$$\Lambda=\frac{1}{\hbar\beta}\sum_{n=-\infty}^{\infty}\frac{1}{\omega_0^2+\nu_n^2+|\nu_n|\hat{\gamma}(|\nu_n|)} ,\qquad \Omega=\frac{1}{\hbar\beta}\sum_{n=-\infty}^{\infty}\frac{\omega_0^2+|\nu_n|\hat{\gamma}(|\nu_n|)}{\omega_0^2+\nu_n^2+|\nu_n|\hat{\gamma}(|\nu_n|)} , \tag{A2}$$

$$C_1(s)=\frac{1}{\hbar\beta\Lambda}\sum_{n=-\infty}^{\infty}\frac{g_n(s)}{\omega_0^2+\nu_n^2+|\nu_n|\hat{\gamma}(|\nu_n|)} ,\qquad C_2(s)=\frac{1}{\hbar\beta}\sum_{n=-\infty}^{\infty}\frac{f_n(s)}{\omega_0^2+\nu_n^2+|\nu_n|\hat{\gamma}(|\nu_n|)} , \tag{A3}$$

and

$$R'(s,u)=-\Lambda C_1(s)C_1(u) +\frac{1}{\hbar\beta}\sum_{n=-\infty}^{\infty}\frac{g_n(s)g_n(u)-f_n(s)f_n(u)}{\omega_0^2+\nu_n^2+|\nu_n|\hat{\gamma}(|\nu_n|)} , \tag{A4}$$

with

$$g_n(s)=\frac{1}{M}\int_0^\infty\frac{d\omega}{\pi}J(\omega)\frac{2\omega}{\omega^2+\nu_n^2}\cos(\omega s) ,\qquad f_n(s)=\frac{1}{M}\int_0^\infty\frac{d\omega}{\pi}J(\omega)\frac{2\omega}{\omega^2+\nu_n^2}\sin(\omega s) . \tag{A5}$$

In the above expression the functions $J(\omega)$ and $\hat{\gamma}(z)$ are given by Eqs. (2.17) and (2.23), respectively. Note that if we set $J(\omega)=0$, the above correlated initial state reduces to the factorized initial state, $\rho_g^{\rm FS}(q_i,q_i')=\langle q_i|\exp(-\beta H_g)|q_i'\rangle$.

APPENDIX B: DERIVATION OF THE PHASE FUNCTION

In this appendix we evaluate the propagating function in Eq. (2.19):

$$\exp\left[\frac{i}{\hbar}\Sigma_t(x_f,r_f,t;x_i,r_i,0)\right]\equiv\int_{x(0)=x_i}^{x(t)=x_f}D[x]\int_{r(0)=r_i}^{r(t)=r_f}D[r]\times\exp\left[\frac{i}{\hbar}\Sigma_t[x,r,t;x_i,r_i,0]\right], \tag{B1}$$

where

$$\Sigma_t[x,r,t;x_i,r_i,0]=\int_0^t ds\, M\left[\dot{x}(s)\dot{r}(s)-\omega_0^2x(s)r(s)-x(s)\frac{d}{ds}\int_0^s du\,\gamma(s-u)r(u)\right]+\frac{i}{2}M\int_0^t ds\int_0^t du\,R(s,u)x(s)x(u)$$
$$+\int_0^t ds[r_iC_1(s)-ix_iC_2(s)]x(s)+\int_0^t ds[F_\alpha^{(n)}(s)x(s)+f_\alpha^{(n)}(s)r(s)+\Phi_\alpha^{(n)}(s)]\ , \tag{B2}$$

with

$$R(s,u)=R'(s,u)+K'(s-u)/M\ , \tag{B3}$$

in which $R'(s,u)$ and $K'(s-u)$ are given in Eqs. (A4) and (2.16). Despite the existence of the phase force $f_\alpha^{(n)}(s)$, our system is still a harmonic system, and only the minimal path of the action contributes to the functional integration of Eq. (B1). We can thus evaluate Eq. (B1) by obtaining the minimal path of the action, which is the solution of the equation of motion

$$\ddot{r}+\frac{d}{ds}\int_0^s du\,\gamma(s-u)r(u)+\omega_0^2r=\frac{1}{M}\overline{F_\alpha^{\prime(n)}}(s)+i\left[\frac{1}{M}\overline{F_\alpha^{\prime\prime(n)}}(s)+\int_0^t du\,R(s,u)x(u)\right], \tag{B4}$$

$$\ddot{x}-\frac{d}{ds}\int_s^t du\,\gamma(u-s)x(u)+\omega_0^2x=\frac{1}{M}f_\alpha^{(n)}(s)\ , \tag{B5}$$

where

$$\overline{F_\alpha^{\prime(n)}}(s)=F_\alpha^{(n)}(s)+Mr_iC_1(s)\ ,\quad i\overline{F_\alpha^{\prime\prime(n)}}(s)=ix_iC_2(s)]\ . \tag{B6}$$

The above equations are readily obtained from the phase Eq. (B2) by taking the variation of $x(s)$ and $r(s)$. Except for the phase force $f_\alpha^{(n)}(s)$, the following procedure is parallel to that of Ref. [3]. We split the minimal action path $r(s)$ into the real and the imaginary parts $r'(s)+ir''(s)$, where $r''(t)=r''(0)=0$ and $r'(s)$ and $r(s)$ satisfy the real and imaginary part of the equation of motion (B4), respectively. With a help of the integration by part, substituting Eqs. (B4) and (B5) into (B2) yields

$$\Sigma_t(x_f,r_f,t;x_i,r_i,0)=M(x_f\dot{r}_f'-x_i\dot{r}_i')+i\int_0^t ds\,x(s)\times\left[\overline{F_\alpha^{\prime\prime(n)}}(s)+\frac{M}{2}\int_0^t ds\,R(s,u)x(u)\right]+\int_0^t ds\,f_\alpha^{(n)}(s)r'(s)+\int_0^t ds\,\Phi_\alpha^{(n)}(s)\ . \tag{B7}$$

The solutions of the real part of Eqs. (B4) and (B5) are written as

$$r'(s)=r_i'\left[\dot{G}_+(s)-\frac{G_+(s)}{G_+(t)}\dot{G}_+(t)\right]+r_f'\frac{G_+(s)}{G_+(t)}-\frac{1}{M}\frac{G_+(s)}{G_+(t)}\int_0^t du\,G_+(t-u)\overline{F_\alpha^{\prime(n)}}(u)+\frac{1}{M}\int_0^s du\,G_+(s-u)\overline{F_\alpha^{\prime(n)}}(u) \tag{B8}$$

and

$$x(s)=x_i\frac{G_+(t-s)}{G_+(t)}+x_f\left[\dot{G}_+(t-s)-\frac{G_+(t-s)}{G_+(t)}\dot{G}_+(t)\right]-\frac{1}{M}\frac{G_+(t-s)}{G_+(t)}\int_0^t du\,G_+(u)f_\alpha^{(n)}(u)+\frac{1}{M}\int_s^t du\,G_+(u-s)f_\alpha^{(n)}(u)\ , \tag{B9}$$

where $G_+(s)$ is expressed by using the Fourier transformation of $\gamma(s)$ as

$$G_+(s)=\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\frac{\omega\tilde{\gamma}(\omega)}{(\omega_0^2-\omega^2)^2+\omega^2\tilde{\gamma}^2(\omega)}\sin(\omega s)\ . \tag{B10}$$

Note that the function $G_+(s)$ relates to the antisymmetrized correlation function at the ground equilibrium state in the form

$$\chi(s)\equiv\frac{i}{\hbar}\langle q(s)q-qq(s)\rangle_g=\frac{1}{M}G_+(s)\ . \tag{B11}$$

By substituting the solutions (B8) and (B9) into (B2), and after a straightforward though tedious, calculation, we recast the phase function in the form

$$\exp\left[\frac{i}{\hbar}\Sigma_t(x_f,r_f,t;x_i,r_i,0)\right]=\frac{1}{N(t)}\exp[i\alpha(t)r_ix_i+i\beta(t)r_ix_f+i\delta(t)r_i-\epsilon(t)x_i^2+i\phi(t)x_ir_f$$
$$+i\psi(t)x_ix_f+\zeta(t)x_i+\kappa(t)x_f+i\sigma(t)r_f+i\tau(t)x_fr_f+c'(t)+ic''(t)]\ , \quad \text{(B12)}$$

where the auxiliary functions are expressed as

$$\alpha(t)=\frac{M}{\hbar^2\Lambda}\frac{S(t)}{\chi(t)}\ , \quad \text{(B13)}$$

$$\beta(t)=\frac{M^2}{\hbar^2\Lambda\chi(t)}[\chi(t)\dot S(t)-\dot\chi(t)S(t)]\ , \quad \text{(B14)}$$

$$\delta(t)=\frac{M}{\hbar^2\Lambda\chi(t)}\int_0^t du\,[\chi(t)S(u)-\chi(u)S(t)]f_\alpha^{(n)}(u)\ , \quad \text{(B15)}$$

$$\epsilon(t)=\frac{\Lambda}{2\hbar M\chi^2(t)}\left[1-\frac{M^2}{\hbar^2\Lambda^2}S^2(t)\right]-\frac{M\Omega}{2\hbar}\ , \quad \text{(B16)}$$

$$\phi(t)=-\frac{1}{\hbar}\frac{1}{\chi(t)}\ , \quad \text{(B17)}$$

$$\psi(t)=\frac{M^2}{\hbar^3\Lambda\chi^2(t)}\left[\frac{\hbar^2\Lambda^2}{M^2}\dot\chi(t)+\chi(t)S(t)\dot S(t)-\dot\chi(t)S^2(t)\right]\ , \quad \text{(B18)}$$

$$\zeta(t)=\frac{i}{\hbar\chi(t)}\int_0^t du\,\chi(t-u)F_\alpha^{(n)}(u)+\frac{1}{\hbar^2\chi(t)}\int_0^t du\left[\frac{M}{\hbar\Lambda}S(t)S(u)-S(t-u)\right]f_\alpha^{(n)}(u)$$
$$+\frac{\Lambda}{\hbar M\chi^2(t)}\left[1-\frac{M^2}{\hbar^2\Lambda^2}S^2(t)\right]\int_0^t du\,\chi(u)f_\alpha^{(n)}(u)\ , \quad \text{(B19)}$$

$$k(t)=\frac{iM}{\hbar\chi(t)}\int_0^t du\,[\chi(t)\dot\chi(t-u)-\dot\chi(t)\chi(t-u)]F_\alpha^{(n)}(u)-\frac{M}{\hbar^2\chi(t)}\int_0^t du\,[\chi(t)\dot S(t-u)-\dot\chi(t)S(t-u)]f_\alpha^{(n)}(u)$$
$$+\frac{1}{\hbar}\beta(t)\int_0^t du\,S(u)f_\alpha^{(n)}(u)-\psi(t)\int_0^t du\,\chi(u)f_\alpha^{(n)}(u)\ , \quad \text{(B20)}$$

$$\sigma(t)=\frac{1}{\hbar\chi(t)}\int_0^t du\,\chi(u)f_\alpha^{(n)}(u)\ , \quad \text{(B21)}$$

$$\nu(t)=-\frac{M}{2\hbar}\left[\Omega-\frac{M^2}{\hbar^2\Lambda\chi^2(t)}[\chi(t)\dot S(t)-\dot\chi(t)S(t)]^2+\Lambda\frac{\dot\chi^2(t)}{\chi^2(t)}\right]\ , \quad \text{(B22)}$$

$$\tau(t)=\frac{M}{\hbar}\frac{\dot\chi(t)}{\chi(t)}\ , \quad \text{(B23)}$$

$$ic'(t)=\frac{i}{\hbar}\int_0^t ds\left[\Phi_\alpha^{(n)}(s)+f_\alpha^{(n)}(s)\int_0^s du\,\chi(s-u)F_\alpha^{(n)}(u)\right]-\frac{i}{\hbar\chi(t)}\int_0^t ds\int_0^t du\,\chi(s)\chi(t-u)f_\alpha^{(n)}(s)F_\alpha^{(n)}(u)\ , \quad \text{(B24)}$$

$$c''(t)=-\frac{1}{2\hbar^2}\int_0^t ds\int_0^t du\,S(s-u)f_\alpha^{(n)}(s)f_\alpha^{(n)}(u)+\frac{M}{2\hbar^3\Lambda\chi^2(t)}\left[\int_0^t du\,[\chi(t)S(u)-S(t)\chi(u)]f_\alpha^{(n)}(u)\right]^2$$
$$-\frac{2M}{\hbar\chi(t)}\int_0^t ds\int_0^t du\,\chi(s)S(t-u)f_\alpha^{(n)}(s)f_\alpha^{(n)}(u)+\frac{\Lambda}{\chi^2(t)}\int_0^t ds\int_0^t du\,\chi(s)\chi(u)f_\alpha^{(n)}(s)f_\alpha^{(n)}(u)\ , \quad \text{(B25)}$$

and

$$N(t)=2\pi\hbar|\chi(t)|\left[\frac{2\pi\hbar\Lambda}{M}\right]^{1/2}\ . \quad \text{(B26)}$$

APPENDIX C: THE AUXILIARY FUNCTIONS

The function Eq. (4.11) is given by

$$g_\pm(t)=\xi^2\int_0^t dt'\int_0^{t'}dt''\left[S(t'')\pm\frac{i\hbar}{2}\chi(t'')\right]\ , \quad \text{(C1)}$$

where $g_-(t)=g_+^*(t)$ and

$$\lambda=\frac{MD^2\omega_0^2}{2\hbar},\quad \xi=\frac{MD\omega_0^2}{\hbar}\ , \quad \text{(C2)}$$

and the antisymmetrized and symmetrized position correlation functions of the ground equilibrium state are given by

$$\chi(t)\equiv\frac{i}{\hbar}\langle q(t)q-qq(t)\rangle_g$$
$$=\frac{1}{M}\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\frac{\omega\tilde\gamma(\omega)}{(\omega_0^2-\omega^2)^2+\omega^2\tilde\gamma^2(\omega)}\sin(\omega t) \quad \text{(C3)}$$

and

$$S(t)\equiv\frac{1}{2}\langle q(t)q+qq(t)\rangle_g$$
$$=\frac{\hbar}{M}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{\omega\tilde{\gamma}(\omega)}{(\omega_0^2-\omega^2)^2+\omega^2\tilde{\gamma}^2(\omega)}\times\coth\left[\frac{\beta\hbar\omega}{2}\right]\cos(\omega t)\ , \qquad (C4)$$

respectively.

If we introduce

$$M(t)\equiv\frac{S(t)}{S(0)} \qquad (C5)$$

and

$$M'(t)\equiv 1-M\omega_0^2\int_0^t dt'\chi(t')$$
$$=\int_{-\infty}^{\infty}\frac{d\omega}{\pi}\frac{\omega_0^2\tilde{\gamma}(\omega)}{(\omega_0^2-\omega^2)^2+\omega^2\tilde{\gamma}^2(\omega)}\cos(\omega t)\ , \qquad (C6)$$

Eq. (C1) can be rewritten as

$$g_{\pm}(t)=\pm i\lambda\left[t-\int_0^t dt'M'(t')\right]+\Delta^2\int_0^t dt'\int_0^{t'}dt''M(t'')\ , \qquad (C7)$$

where we put and $\Delta^2=2\lambda M\omega_0^2S(0)/\hbar$.

As is well known, the antisymmetrized correlation function is related to the symmetrized function by the fluctuation-dissipation theorem. If we denote the Fourier transform of $S(t)$ and $\chi(t)$ by $S[\omega]$ and $\chi[\omega]$, we have [3]

$$S[\omega]=\hbar\coth\left[\frac{\omega\hbar\beta}{2}\right]\chi''[\omega]\ , \qquad (C8)$$

where $\chi''[\omega]$ is the imaginary part of $\chi[\omega]$. For the Fourier transforms of $M(t)$ and $M'(t)$, which are denoted by $M[\omega]$ and $M'[\omega]$, the fluctuation-dissipation theorem assumes the form

$$\Delta^2M[\omega]=\lambda\omega\coth\left[\frac{\omega\hbar\beta}{2}\right]M'[\omega]\ . \qquad (C9)$$

This result can be obtained from the cummulant expansion method [5]. At high temperatures, $\hbar\beta\omega\ll 1$, we have $\Delta^2=2\lambda/\beta\hbar$ and $M(t)=M'(t)$.

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