Phase-space algorithm for simulating quantum nonlinear response functions of bosons using stochastic classical trajectories

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Using the positive P-representation of the density matrix, we develop an algorithm for calculating the quantum many-body nonlinear response functions of a system of bosons driven impulsively by external fields. The formalism maps the quantum time evolution of N boson degrees of freedom into a stochastic dynamics of $4N$ classical degrees of freedom. The first- and the third-order response functions are calculated by propagating the parameters of the P-representation using a set of coupled Langevin equations with multiplicative noise. These parameters serve as classical variables. Two classical ways for computing the response functions are presented. In the nonequilibrium method, an observable is calculated for weak impulsive pulses, and the response functions are obtained by taking its derivatives with respect to the pulse amplitudes. In the alternative, equilibrium simulation, the response functions are expressed in terms of time-correlation functions involving the P-representation parameters and stability matrices representing the perturbation of the trajectories. The stability matrices can be propagated simultaneously with the Langevin equations for the parameters. The formalism is generalized for a many-body boson system coupled to a harmonic bath.

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I. INTRODUCTION

The computational cost of quantum response functions scales exponentially with the number of degrees of freedom since it requires the calculation of the many body states [1–4]. These response functions are given by specific combinations of multipoint correlations functions. The scaling is much more favorable (power law) for classical systems. Two algorithms based on classical molecular dynamics (MD) simulations have been employed: one uses nonequilibrium simulations based on trajectories of the externally driven system [5]. The alternative stability matrix approach uses derivatives of positions and momenta in an equilibrium simulation along the trajectories [6,7]. Both procedures have been successfully employed for fifth-order Raman [8–15], second-order surface IR [16], and third-order IR measurements [17–22]. Semiclassical expansions can provide corrections in powers of $\hbar$ to the classical techniques. They work either at high temperature or for weakly anharmonic systems [23–27]. A computationally viable general procedure that includes quantum effects outside these limits will be highly desirable.

In this paper, we propose a fully quantum algorithm based on the coherent state representation of the many-body density matrix developed by Glauber [28] and Drummond and Gardiner [29]. There are several such representations which use different operator ordering prescriptions; normal and antinormal [33,34] or symmetric [35]. We shall work with Husimi's positive P-representation [36], but the same ideas can be applied to the other representations. Gaussian wave packets have been widely used to simulate the wave functions of molecular vibrations [37,38]. The density matrix of quantum states can be represented by a superposition of Gaussian phase-space wave packets [28,29]. The coherent states form an overcomplete basis set offering considerable freedom in the representation. The density matrix satisfies a Fokker-Plank equation in its parameter space ($4N$ for N degrees of freedom). This Fokker-Planck equation is equivalent to classical-like Langevin equations. The quantum system is, thus, mapped rigorously into $4N$ degrees of freedom with stochastic dynamics. Our primary goal is to connect these powerful representations for interacting bosons to nonlinear response theory. The quantum response functions can be calculated in this classical parameter space using the two available classical algorithms described above. Simulations will require sampling of the stochastic forces, and coupling the quantum system to a classical bath poses no difficulty in this approach. The Langevin equations need to be modified to include additional noise sources with only a modest increase in computational cost. The same strategy was recently discussed for fermions. [39]

The paper is divided as follows. In Sec. II, we review the P-representation for interacting bosons. We also derive the Langevin equations for the P-representation parameters driven by an external field. Section III connects the P-representation with the response function formalism. We show how the nonequilibrium simulation can be combined with the Langevin equations to calculate nonlinear response functions. We also derive alternative expressions using the equilibrium correlation functions for the optical response by employing the stability matrices. We demonstrate how these two approaches differ for linear or nonlinear interactions with the external fields. In Sec. IV, the method is generalized to include coupling with a harmonic bath. Sec. V compares the computational cost of the nonequilibrium and the stability matrix approaches. Concluding remarks are given in Sec. VI.

II. P-REPRESENTATION

We consider a system of N boson degrees of freedom driven by an external field and described by the Hamiltonian

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$$\hat{H}(t) = \omega_{nm}\hat{a}_n^\dagger \hat{a}_m + \kappa_{nm,kl}\hat{a}_n^\dagger \hat{a}_m^\dagger \hat{a}_k \hat{a}_l - \epsilon(t)[\mu_n \hat{a}_n + \mu_n^* \hat{a}_n^\dagger + \mu_n^{(2)} \hat{a}_n^\dagger \hat{a}_n \hat{a}_n + (\mu_n^{(2)})^* \hat{a}_n^\dagger \hat{a}_n^\dagger \hat{a}_n]. \quad (1)$$

Summation over repeated indices is implied unless specified otherwise, and all indices run from 1 to N. $\hat{a}_n^\dagger$ ($\hat{a}_n$) create (annihilate) an excitation in the mode n. They obey the boson commutation relation

$$[\hat{a}_n^\dagger, \hat{a}_m] = \delta_{n,m}. \quad (2)$$

ω_{nm} denotes the boson energy when $n=m$ and the coupling between them when $n \neq m$. $\kappa_{nm,kl}$ are two-body interactions. Coupled two-level systems (hard core bosons) can be described. κ are taken to be very large when $n=m=k=l$ and zero elsewhere. $\epsilon(t)$ is the external time-dependent driving field, and μ_n and $\mu_n^{(2)}$ are the elements of the dipole operator. κ and $\mu^{(2)}$ are the sources of nonlinearity of the model. When these vanish, the nonlinear response is zero.

The approach proposed by Drummond *et al.* is to expand the density matrix of a many-body bosonic system in coherent state wave functions. [28,29,40] These are expressed in terms of standard harmonic oscillator wave functions [28]

$$||\bar{\alpha}\rangle = ||\alpha_1, \alpha_2, \ldots, \alpha_N\rangle = \exp\left(\sum_{i=1}^{N} \alpha_i \hat{a}_i^\dagger\right)|\bar{0}\rangle, \quad (3)$$

where $|\bar{0}\rangle$ is a vacuum state and $\hat{\mathbf{a}}^\dagger$ is an array containing all the creation operators. The inner product of such wave functions is given by

$$\langle\bar{\beta}^*||\bar{\alpha}\rangle = \exp\left(\sum_{n=1}^{N} \alpha_n \beta_n\right). \quad (4)$$

The positive P-representation is then given by

$$\hat{\rho}(t) = \int d^2\bar{\alpha} d^2\bar{\beta} P(\bar{\alpha}, \bar{\beta}, t)\hat{\Lambda}(\bar{\alpha}, \bar{\beta}), \quad (5)$$

where

$$d^2\bar{\alpha} d^2\bar{\beta} = \prod_n d\alpha_n^x d\alpha_n^y d\beta_n^x d\beta_n^y$$

where the superscripts x (y) refers to the real (imaginary) part. $\hat{\Lambda}(\bar{\alpha}, \bar{\beta})$ is defined as follows:

$$\hat{\Lambda}(\bar{\alpha}, \bar{\beta}) = ||\bar{\alpha}\rangle\langle\bar{\beta}^*||e^{-\bar{\alpha}\cdot\bar{\beta}}, \quad (6)$$

or in terms of the ladder operators,

$$\hat{\Lambda}(\bar{\alpha}, \bar{\beta}) = e^{-\bar{\alpha}\cdot\bar{\beta}+\bar{\alpha}\cdot\hat{\mathbf{a}}^\dagger}|\bar{0}\rangle\langle\bar{0}|e^{\bar{\beta}\cdot\hat{\mathbf{a}}}. \quad (7)$$

$P(\bar{\alpha}, \bar{\beta}, t)$ is normalized such that

$$\int d^2\bar{\alpha} d^2\bar{\beta} P(\bar{\alpha}, \bar{\beta}, t) = 1. \quad (8)$$

The P-representation is not unique. For a given $\hat{\rho}$, there is an infinite number of possible P functions. Drummond *et al.* [29] showed that it is always possible to obtain positive distribution which satisfies the relation

$$P(\bar{\alpha}, \bar{\beta}) = \frac{1}{(4\pi^2)^{N+M}} \exp\left[-\left|\frac{\bar{\alpha} - \bar{\beta}^*}{2}\right|^2\right] \times \left\langle \frac{\bar{\alpha} + \bar{\beta}^*}{2}\middle|\hat{\rho}\middle|\frac{\bar{\alpha} + \bar{\beta}^*}{2}\right\rangle, \quad (9)$$

where $||\bar{\alpha}\rangle = e^{-\bar{\alpha}\cdot\bar{\alpha}/2}|\bar{\alpha}\rangle$. When a creation or annihilation operators act on $\hat{\Lambda}$, we have

$$\hat{a}_n\hat{\Lambda}(\bar{\alpha}, \bar{\beta}) = \alpha_n\hat{\Lambda}(\bar{\alpha}, \bar{\beta}), \quad (10a)$$

$$\hat{\Lambda}(\bar{\alpha}, \bar{\beta})\hat{a}_n = \left(\alpha_n + \frac{\partial}{\partial\beta_n}\right)\hat{\Lambda}(\bar{\alpha}, \bar{\beta}), \quad (10b)$$

$$\hat{a}_n^\dagger\hat{\Lambda}(\bar{\alpha}, \bar{\beta}) = \left(\beta_n + \frac{\partial}{\partial\alpha_n}\right)\hat{\Lambda}(\bar{\alpha}, \bar{\beta}), \quad (10c)$$

and

$$\hat{\Lambda}(\bar{\alpha}, \bar{\beta})\hat{a}_n^\dagger = \beta_n\hat{\Lambda}(\bar{\alpha}, \bar{\beta}). \quad (10d)$$

The time evolution of the density matrix is described by Liouville's equation

$$\frac{\partial\hat{\rho}(t)}{\partial t} = \frac{-i}{\hbar}[\hat{H}(t), \hat{\rho}(t)], \quad (11)$$

where $\hat{H}(t)$ is the Hamiltonian of the system. Using the above representation, we obtain

$$\int d^2\bar{\alpha} d^2\bar{\beta}\frac{\partial P(\bar{\alpha}, \bar{\beta}, t)}{\partial t}\hat{\Lambda}(\bar{\alpha}, \bar{\beta}) = \frac{-i}{\hbar}\int d^2\bar{\alpha} d^2\bar{\beta} P(\bar{\alpha}, \bar{\beta}, t)[\hat{H}(t), \hat{\Lambda}(\bar{\alpha}, \bar{\beta})]. \quad (12)$$

When the last commutator is evaluated by combining Eqs. (10a)–(10d) with Eq. (1), we obtain

$$\dot{\hat{\rho}}(t) = \int d^2\bar{\alpha} d^2\bar{\beta}\frac{\partial P(\bar{\alpha}, \bar{\beta}, t)}{\partial t}\hat{\Lambda}(\bar{\alpha}, \bar{\beta}) = \int d^2\bar{\alpha} d^2\bar{\beta} P(\bar{\alpha}, \bar{\beta}, t)\left(A_n\frac{\partial}{\partial\alpha_n} + B_n\frac{\partial}{\partial\beta_n} + \frac{1}{2}G_{A,nk}G_{A,mk}\frac{\partial^2}{\partial\alpha_n\,\partial\,\alpha_m} + \frac{1}{2}G_{B,nk}G_{B,mk}\frac{\partial^2}{\partial\beta_n\,\partial\,\beta_m}\right)\hat{\Lambda}(\bar{\alpha}, \bar{\beta}), \quad (13)$$

where

$$A_n = A_n^x + iA_n^y$$
$$= -\frac{i}{\hbar}\left(\sum_m \omega_{nm}\alpha_m + \sum_{m,k,l}\left[\kappa_{nm,kl}\alpha_k\alpha_l\beta_m + \kappa_{mn,kl}\alpha_k\alpha_l\beta_m\right] - \epsilon(t)\mu_n^* - \epsilon(t)\mu_n^{(2)}\alpha_n^2 - 2\epsilon(t)(\mu_n^{(2)})^*\alpha_n\beta_n\right), \quad (14)$$

$$B_n = B_n^x + iB_n^y$$
$$= \frac{i}{\hbar}\left(\sum_m \omega_{mn}\beta_m + \sum_{m,k,l}\left[\kappa_{kl,mn}\beta_k\beta_l\alpha_m + \kappa_{kl,nm}\beta_k\beta_l\alpha_m\right] - \epsilon(t)\mu_n - \epsilon(t)(\mu_n^{(2)})^*\beta_n^2 - 2\epsilon(t)\mu_n^{(2)}\alpha_n\beta_n\right), \quad (15)$$

and

$$\sum_k G_{A,nk}G_{A,mk} = -\frac{2i}{\hbar}\left(\sum_{k,l}\left[\kappa_{nm,kl}\alpha_k\alpha_l\right] - \epsilon(t)(\mu_n^{(2)})^*\alpha_n\delta_{n,m}\right), \quad (16)$$

$$\sum_k G_{B,nk}G_{B,mk} = \frac{2i}{\hbar}\left(\sum_{k,l}\left[\kappa_{kl,nm}\beta_k\beta_l\right] - \epsilon(t)\mu_n^{(2)}\beta_n\delta_{n,m}\right). \quad (17)$$

In these last four equations, we wrote all sums explicitly for clarity. G_A and G_B are complex matrices obtained taking the square root of the symmetric complex matrix defined by the right-hand side of Eqs. (16) and (17) (we assumed that $\kappa_{kl,nm}$ was symmetric under the permutation of n and m and of k and l). Clearly, Eqs. (16) and (17) do not specify G_A and G_B completely. The usefulness of this extra freedom was analyzed in Ref. [30]. Here, the choice made by Deuar *et al.* [31] is assumed and the positive square root is chosen.

Since $\hat{\Lambda}(\alpha,\beta)$ is analytic in the complex plane, the derivative acting on $\hat{\Lambda}(\alpha,\beta)$ in Eq. (13) can be chosen with some freedom. For example,

$$\frac{\partial}{\partial\alpha} = \frac{\partial}{\partial\alpha^x} = -i\frac{\partial}{\partial\alpha^y}.$$

We use this freedom to require that all coefficients in Eq. (13) be real. For example,

$$A_n\frac{\partial}{\partial\alpha_n} = A_n^x\frac{\partial}{\partial\alpha^x} + A_n^y\frac{\partial}{\partial\alpha^y}. \quad (18)$$

Even if A_n is a complex quantity, we use the freedom in $\partial/\partial\alpha_n$ to make the product $A_n\partial/\partial\alpha_n$ real. Equation (13) is then integrated by parts, and a Fokker-Planck equation for the time dependence of $P(\bar{\alpha},\bar{\beta},t)$ is obtained as

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial\alpha_n^x}A_n^xP - \frac{\partial}{\partial\alpha_n^y}A_n^yP - \frac{\partial}{\partial\beta_n^x}B_n^xP - \frac{\partial}{\partial\beta_n^y}B_n^yP + \frac{1}{2}\left[\frac{\partial^2}{\partial\alpha_n^x\,\partial\,\alpha_m^x}G_{A,nk}^xG_{A,mk}^xP + \frac{\partial^2}{\partial\alpha_n^y\,\partial\,\alpha_m^y}G_{A,nk}^yG_{A,mk}^yP + 2\frac{\partial^2}{\partial\alpha_n^y\,\partial\,\alpha_m^x}G_{A,nk}^yG_{A,mk}^xP\right] + \frac{1}{2}\left[\frac{\partial^2}{\partial\beta_n^x\,\partial\,\beta_m^x}G_{B,nk}^xG_{B,mk}^xP + \frac{\partial^2}{\partial\beta_n^y\,\partial\,\beta_m^y}G_{B,nk}^yG_{B,mk}^yP + 2\frac{\partial^2}{\partial\beta_n^y\,\partial\,\beta_m^x}G_{B,nk}^yG_{B,mk}^xP\right]. \quad (19)$$

Given an initial distribution of the complex variables α_n and β_n, the time evolution can be computed by employing the exact mapping between Fokker-Planck and Langevin equations. Using Ito calculus (for a review of the difference between Ito and Stratonovitch stochastic integrations, see [32]), we obtain the Langevin equations

$$\frac{d\alpha_n^x}{dt} = A_n^x + G_{A,nm}^x\xi_m^\ddagger(t) \quad (20a)$$

$$\frac{d\alpha_n^y}{dt} = A_n^y + G_{A,nm}^y\xi_m^\ddagger(t) \quad (20b)$$

$$\frac{d\beta_n^x}{dt} = B_n^x + G_{B,nm}^x\eta_m^\ddagger(t) \quad (20c)$$

$$\frac{d\beta_n^y}{dt} = B_n^y + G_{B,nm}^y\eta_m^\ddagger(t), \quad (20d)$$

where $\xi_n^\ddagger(t)$ and $\eta_n^\ddagger(t)$ are uncorrelated white noise variables, $\langle\xi_n^\ddagger(t)\xi_n^\ddagger(t')\rangle = \langle\eta_n^\ddagger(t)\eta_n^\ddagger(t')\rangle = \delta(t-t')$, $\langle\xi_n^\ddagger(t)\eta_m^\ddagger(t')\rangle = 0$ for all n and m, and $\langle\xi_n^\ddagger(t)\xi_m^\ddagger(t')\rangle = \langle\eta_n^\ddagger(t)\eta_m^\ddagger(t')\rangle = 0$ for $n \neq m$. Since $G_{A(B)}$ depends on $\bar{\alpha}(\bar{\beta})$, the noise in these equations is multiplicative. Numerical algorithm for the integration of differential equations with multiplicative noise are given in Ref. [41]. The evaluation of $G_{A(B)}$ may also cause numerical difficulties because it involves the diagonalization of a complex matrix that depends on $\alpha(\beta)$. This diagonalization should be performed at every time step for the integration of Eqs. (20a)–(20d). The distribution function $P(\bar{\alpha},\bar{\beta},t)$ can be reconstructed from an ensemble average over trajectories which are obtained from Eqs. (20a)–(20d). The initial conditions are sampled from $P(\bar{\alpha},\bar{\beta},0)$. The formalism maps the quantum time evolution of N boson degrees of freedom into a stochastic dynamics of freedom of $4N$ classical degrees of freedom. Note that, in a classical mechanics sense, α and β would be conjugate variables in the absence of the noise (if $G_A = G_B = 0$).

III. RESPONSE FUNCTIONS

In this section, we apply the above formalism to the calculation of nonlinear optical response functions for many degrees of freedom. Hereafter we consider the optical re-

sponse to an external electric field but the formalism can be applied to any externally driven system.

A. Linear interaction with the field

We consider the linear interaction with the external field by assuming $\mu_n^{(2)}=0$ in Eq. (1). In optical spectroscopy, the measured signal is directly related to the average polarization

$$\mathcal{P}(t) = \mathrm{Tr}[(\mu_n \hat{a}_n + \mu_n^* \hat{a}_n^\dagger)\hat{\rho}(t)], \tag{21}$$

where Tr stands for trace. Using the coherent states representation, the polarization becomes

$$\mathcal{P}(t) = \int d\bar{\alpha} P(\bar{\alpha},t) c_{n,q} \alpha_{n,q}, \tag{22}$$

where $\bar{\alpha}$ contains all $\alpha_{n,q}$'s, and

$$\alpha_{n,1} = \alpha_n^x, \quad \alpha_{n,2} = \alpha_n^y, \quad \alpha_{n,3} = \beta_n^x, \quad \alpha_{n,4} = \beta_n^y$$

and

$$c_{n,1} = \mu_n, \quad c_{n,2} = i\mu_n, \quad c_{n,3} = \mu_n^*, \quad c_{n,4} = i\mu_n^*.$$

Note that q runs from 1 to 4. $P(\bar{\alpha},t)$ is obtained by solving the Fokker-Planck Eq. (19). The polarization can be equivalently calculated using a path integral over trajectories of $\alpha_{n,q}(t)$ given an initial distribution [described by $P_0(\bar{\alpha})$] and a noise history (described by $J[\bar{\xi}^\ddagger(t), \bar{\eta}^\ddagger(t)]$),

$$\mathcal{P}(t) = \int d\bar{\alpha} \int \mathcal{D}[\bar{\eta}^\ddagger(t)]\mathcal{D}[\bar{\xi}^\ddagger(t)] \times P_0(\bar{\alpha}) J[\bar{\xi}^\ddagger(t), \bar{\eta}^\ddagger(t)] c_{n,q} \alpha_{n,q}(t). \tag{23}$$

The noise variables $\bar{\xi}^\ddagger(t)$ and $\bar{\eta}^\ddagger(t)$ contain all the $\eta_n^\ddagger(t)$'s and $\xi_n^\ddagger(t)$'s. Mathematically, the noise history is described as follows:

$$J[\bar{\xi}^\ddagger(t), \bar{\eta}^\ddagger(t)] \propto e^{-1/2\int_0^t d\tau (\bar{\xi}^\ddagger(\tau)\cdot\bar{\xi}^\ddagger(\tau) + \bar{\eta}^\ddagger(\tau)\cdot\bar{\eta}^\ddagger(\tau))} \tag{24}$$

and is normalized such that

$$\int \mathcal{D}[\bar{\eta}^\ddagger(t)]\mathcal{D}[\bar{\xi}^\ddagger(t)] J(\bar{\xi}^\ddagger(t), \bar{\eta}^\ddagger(t)) = 1. \tag{25}$$

This result gives the polarization to all orders in the external fields. The response functions are derived by expanding the polarization perturbatively in terms of the external fields,

$$\mathcal{P}(t) = \sum_{n=1}^{\infty} \int_0^\infty dt_n \ldots \int_0^\infty dt_1 S^{(n)}(t_n, t_{n-1}, \ldots, t_1) \times \epsilon(t-t_n)\epsilon(t-t_n-t_{n-1}) \ldots \epsilon(t-t_n-t_{n-1}\ldots-t_1), \tag{26}$$

where $S^{(n)}(t_n, t_{n-1}, \ldots, t_1)$ is the nth-order response function.

In a four-wave mixing experiment, the signal is related to the third-order response function. We shall outline how the response functions up to third order can be calculated from the Langevin Eqs. (20a)–(20d). We assume delta function pulses for the external fields

$$\epsilon(t) = \epsilon_1 \delta(t-\tau_1) + \epsilon_2 \delta(t-\tau_2) + \epsilon_3 \delta(t-\tau_3), \tag{27}$$

where ϵ_i is the amplitude of the ith pulse and $\tau_3 > \tau_2 > \tau_1$. From Eq. (26), we have

$$S^{(1)}(t-\tau_1) = \left(\frac{\partial}{\partial \epsilon_1} \mathcal{P}(t) \right)_{\epsilon_1=\epsilon_2=\epsilon_3=0}, \tag{28a}$$

$$S^{(2)}(t-\tau_2, \tau_2-\tau_1) = \left(\frac{\partial^2}{\partial \epsilon_2 \, \partial \, \epsilon_1} \mathcal{P}(t) \right)_{\epsilon_1=\epsilon_2=\epsilon_3=0}, \tag{28b}$$

and

$$S^{(3)}(t-\tau_3, \tau_3-\tau_2, \tau_2-\tau_1) = \left(\frac{\partial^3}{\partial \epsilon_3 \, \partial \, \epsilon_2 \, \partial \, \epsilon_1} \mathcal{P}(t) \right)_{\epsilon_1=\epsilon_2=\epsilon_3=0}. \tag{28c}$$

When a system is subjected to the pulses, the trajectories make a jump, i.e, at time τ_1,

$$\alpha_{n,q}(\tau_1^+) = \alpha_{n,q}(\tau_1^-) + \frac{\epsilon_1 \mu_{n,q}}{\hbar}, \tag{29}$$

where $\mu_{n,q}$ is defined as

$$\mu_{n,1} = \mu_n^y, \quad \mu_{n,2} = \mu_n^x, \quad \mu_{n,3} = \mu_n^y, \quad \mu_{n,4} = -\mu_n^x.$$

We further denote by $\bar{\mu}$ the array containing all $\mu_{n,q}$'s. Similar jump conditions are induced by the pulses that act at τ_2 and τ_3. Hence, the value of $\alpha_{n,q}$ at time t is generally given by

$$\alpha_{n,q}(t) = F_{n,q}\left(t-\tau_3, \bar{F}\left\{ \tau_3-\tau_2, \bar{F}\left[\tau_2-\tau_1, \bar{\alpha}(\tau_1) + \frac{\epsilon_1 \bar{\mu}}{\hbar} \right] + \frac{\epsilon_2 \bar{\mu}}{\hbar} \right\} + \frac{\epsilon_3 \bar{\mu}}{\hbar} \right), \tag{30}$$

where $\bar{F}[t-\tau_1, \bar{\alpha}(\tau_1)]$ is a function that takes $\bar{\alpha}(\tau_1)$ and propagates it from τ_1 to $t-\tau_1$ in the absence of any fields (this function certainly depends on the noise history, but this dependence was not explicitly written in the argument of the function for simplicity).

As an example, we show how this approach can be used to calculate the linear response function. According to Eqs. (28a) and (23), $S^{(1)}(t-\tau_1)$ is given by

$$S^{(1)}(t-\tau_1) = \lim_{\epsilon_1 \to 0} \frac{1}{\epsilon_1} \int d\bar{\alpha} \int \mathcal{D}[\bar{\xi}^\ddagger(t)]\mathcal{D}[\bar{\eta}^\ddagger(t)] \times P_0(\bar{\alpha}) J(\bar{\xi}^\ddagger(t), \bar{\eta}^\ddagger(t)) c_{n,q} \left\{ F_{n,q}\left[t-\tau_1, \bar{\alpha}(\tau_1) + \frac{\epsilon_1 \bar{\mu}}{\hbar} \right] - F_{n,q}[t-\tau_1, \bar{\alpha}(\tau_1)] \right\}, \tag{31}$$

where $\bar{\alpha}(\tau_1)$ has been propagated from 0 to τ_1 in the absence of fields. When the terms inside the brackets are expanded in powers of the field amplitude, it gives

$$S^{(1)}(t-\tau_1)=\int d\bar{\alpha}\int \mathcal{D}[\bar{\eta}^{\ddagger}(t)]\mathcal{D}[\bar{\xi}^{\ddagger}(t)]P_0(\bar{\alpha})J(\bar{\xi}^{\ddagger}(t),\bar{\eta}^{\ddagger}(t)) \times\frac{\partial F_{n_1,q_1}(t-\tau_1,\bar{\alpha}(\tau_1))}{\partial\alpha_{n_2,q_2}(\tau_1)}\frac{c_{n_1,q_1}\mu_{n_2,q_2}}{\hbar}, \tag{32}$$

which can be written in compact notation as

$$S^{(1)}(t-\tau_1)=\frac{c_{n_1,q_1}\mu_{n_2,q_2}}{\hbar}\left\langle\frac{\partial\alpha_{n_1,q_1}(t-\tau_1)}{\partial\alpha_{n_2,q_2}(\tau_1)}\right\rangle. \tag{33}$$

If the distribution function is stationary between 0 and τ_1, we can take $\tau_1=0$. Further, if the system is initially in the ground state (note that the ground state is stationary with respect to the Hamiltonian in the absence of fields), P_0 is given by

$$P_0(\bar{\alpha})=\frac{1}{(4\pi^2)^N}e^{-\frac{1}{2}\Sigma_{n,q}\alpha_{n,q}^2}, \tag{34}$$

and the first order response is simplified to (after an integration by parts)

$$S^{(1)}(t)=\frac{c_{n_1,q_1}\mu_{n_2,q_2}}{\hbar}\langle\alpha_{n_1,q_1}(t)\alpha_{n_2,q_2}(0)\rangle, \tag{35}$$

where $\alpha_{n,q}(t)$ is obtained simulating Eqs. (20a)–(20d) in the *absence* of the fields. The second- and third-order response functions are derived following the same procedure. The resulting expressions are

$$S^{(2)}(t-\tau_2,\tau_2)=\frac{c_{n_1,q_1}\mu_{n_2,q_2}\mu_{n_3,q_3}}{\hbar^2}\langle M_{n_1q_1,n_2q_2}(t,\tau_2)\alpha_{n_3,q_3}(0)\rangle, \tag{36}$$

and

$$\begin{aligned}S^{(3)}(t-\tau_3,\tau_3-\tau_2,\tau_2)=&\frac{c_{n_1,q_1}\mu_{n_2,q_2}\mu_{n_3,q_3}\mu_{n_4,q_4}}{\hbar^3}\\&\times\langle M^{(2)}_{n_1q_1,n_2q_2,n_5q_5}(t,\tau_3,\tau_3)\\&\times M^{(2)}_{n_5q_5,n_3q_3,n_4q_4}(\tau_3,\tau_2,0)\\&+M^{(2)}_{n_1q_1,n_3q_3,n_4q_4}(t,\tau_3,\tau_2)\alpha_{n_2,q_2}(0)\rangle,\end{aligned} \tag{37}$$

where we have again assumed τ_1 to be zero and P_0 to be given by Eq. (34). M and $M^{(2)}$ are stability matrices defined as

$$M_{n_1q_1,n_2q_2}(t_2,t_1)=\frac{\partial\alpha_{n_1,q_1}(t_2)}{\partial\alpha_{n_2,q_2}(t_1)}, \tag{38}$$

and

$$M^{(2)}_{n_1q_1,n_2q_2,n_3q_3}(t_3,t_2,t_1)=\frac{\partial^2\alpha_{n_1,q_1}(t_3)}{\partial\alpha_{n_2,q_2}(t_2)\,\partial\,\alpha_{n_3,q_3}(t_1)}. \tag{39}$$

B. Non-linear interaction with the field

When the dipole moment depends nonlinearly on the oscillator coordinates, the average polarization is generally given by

$$\mathcal{P}(t)=\int d\bar{\alpha}\int \mathcal{D}[\bar{\eta}^{\ddagger}(t)]\mathcal{D}[\bar{\xi}^{\ddagger}(t)]P_0(\bar{\alpha})J[\bar{\xi}^{\ddagger}(t),\bar{\eta}^{\ddagger}(t)]B[\bar{\alpha}(t)], \tag{40}$$

where $B[\bar{\alpha}(t)]$ is nonlinear in the $\alpha_{n,q}$'s. The jump condition expressed by Eq. (29) can be replaced by

$$\alpha_{n,q}(\tau_1^+)=\alpha_{n,q}(\tau_1^-)+\frac{\epsilon_1\mu_{n,q}}{\hbar}+\int_{\tau_1^-}^{\tau_1^+}d\tau G_{nm,q}(\tau)\xi_{m,q}(\tau), \tag{41}$$

where

$$G_{nm,1}=G^x_{A,nm},\quad G_{nm,2}=G^y_{A,nm},$$
$$G_{nm,3}=G^x_{B,nm},\quad G_{nm,4}=G^y_{B,nm},$$

and

$$\xi_{n,1}=\xi_n,\quad \xi_{n,2}=\xi_n,\quad \xi_{n,3}=\eta_n,\quad \xi_{n,4}=\eta_n.$$

We can derive a similar correlation function expression for the optical response following the procedure presented in the last section. It turns out that the stochastic nature of the jump does not contribute to the response function, because it brings a term of the form $\xi^{\ddagger}_{n,i}(\tau_1)$, $\xi^{\ddagger}_{n,i}(\tau_1)\xi^{\ddagger}_{m,j}(\tau_2)$, and $\xi^{\ddagger}_{n,i}(\tau_1)\xi^{\ddagger}_{m,j}(\tau_2)\xi^{\ddagger}_{k,l}(\tau_3)$ which vanishes when the noise is averaged (i.e., the random jumps at different times are uncorrelated). We then obtain

$$S^{(1)}(t)=\frac{\mu_{n,q}}{\hbar}\left\langle\frac{\partial B[\alpha(t)]}{\partial\alpha_{n,q}(\tau_1)}\right\rangle, \tag{42}$$

and under the same assumption as in the last section (the distribution is stationary between 0 and τ_1)

$$S^{(1)}(t)=\frac{\mu_{n,q}}{\hbar}\langle B[\alpha(t)]\alpha_{n,q}(0)\rangle. \tag{43}$$

For the second- and third-order response functions, we obtain

$$\begin{aligned}S^{(2)}(t-\tau_2,\tau_2)=\frac{\mu_{n_1,q_1}\mu_{n_2,q_2}}{\hbar^2}\Bigg\langle&\frac{\partial B(t)}{\partial\alpha_{n_3,q_3}(t)}M^{(2)}_{n_3q_3,n_1q_1,n_2q_2}(t,\tau_2,0)\\&+\frac{\partial^2B(t)}{\partial\alpha_{n_1,q_1}(0)\,\partial\,\alpha_{n_2,q_2}(\tau_2)}\Bigg\rangle,\end{aligned} \tag{44}$$

and

$$S^{(3)}(t-\tau_3,\tau_3-\tau_2,\tau_2)=\frac{\mu_{n_1,q_1}\mu_{n_2,q_2}\mu_{n_3,q_3}}{\hbar^3}\left\langle \frac{\partial^3 B(t)}{\partial\alpha_{n_1,q_1}(\tau_3)\,\partial\,\alpha_{n_2,q_2}(\tau_2)\,\partial\,\alpha_{n_3,q_3}(0)}+\frac{\partial^2 B(t)}{\partial\alpha_{n_4,q_4}(t)\,\partial\,\alpha_{n_1,q_1}(0)}M^{(2)}_{n_4q_4,n_2q_2,n_3q_3}(t,\tau_3,\tau_2)\right.$$
$$+\frac{\partial^2 B(t)}{\partial\alpha_{n_4,q_4}(t)\,\partial\,\alpha_{n_1,q_1}(\tau_2)}M^{(2)}_{n_4q_4,n_2q_2,n_3q_3}(t,\tau_3,0)+\frac{\partial^2 B(t)}{\partial\alpha_{n_4,q_4}(t)\,\partial\,\alpha_{n_1,q_1}(\tau_3)}M^{(2)}_{n_4q_4,n_2q_2,n_3q_3}(t,\tau_2,0)$$
$$+\frac{\partial^2 B(t)}{\partial\alpha_{n_4,q_4}(\tau_3)\,\partial\,\alpha_{n_1,q_1}(\tau_3)}M^{(2)}_{n_4q_4,n_2q_2,n_3q_3}(\tau_3,\tau_2,0)+\frac{\partial B(t)}{\partial\alpha_{n_4,q_4}(t)}M^{(2)}_{n_4q_4,n_5q_5,n_1q_1}(t,\tau_3,\tau_3)M^{(2)}_{n_5q_5,n_2q_2,n_3q_3}(\tau_3,\tau_2,0)$$
$$\left.+\frac{\partial B(t)}{\partial\alpha_{n_4q_4}(t)}\frac{\partial^3\alpha_{n_4q_4}(t)}{\partial\alpha_{n_1q_1}(\tau_3)\,\partial\,\alpha_{n_2q_2}(\tau_2)\,\partial\,\alpha_{n_3q_3}(0)}\right\rangle. \tag{45}$$

When $B(t)$ is linear in the $\alpha_{n,q}$'s, these results reduce to Eqs. (35)–(37). The derivatives of $B(t)$ with respect to $\alpha(\tau)$ for $\tau\neq t$ are evaluated using the first-order stability matrices,

$$\frac{\partial^2 B(t)}{\partial\alpha_{n_1,q_1}(t)\,\partial\,\alpha_{n_2,q_2}(\tau)}=\frac{\partial^2 B(t)}{\partial\alpha_{n_1,q_1}(t)\,\partial\,\alpha_{n_3,q_3}(t)}M_{n_3q_3,n_2q_2}(t,\tau). \tag{46}$$

Note that the results summarized in Eqs. (44) and (45) are very similar to the ones obtained by Dellago and Mukamel [7] and by Saito and Ohmine [12,13] in the calculation of nonlinear response functions for fully classical systems. The advantage of the positive P-representation is that, from classical-like trajectories and correlation function expressions, we obtain fully quantum-mechanical response functions. Note that we did not need to invoke the rotating-wave approximation [2].

C. Simulation protocol

We discuss two general schemes for calculating the nonlinear response functions, the nonequilibrium and the stability matrix approaches. In the nonequilibrium approach, the Langevin equation is simulated for the externally driven systems, and the derivatives appearing in Eqs. (28a)–(28c) are numerically evaluated. The simulation goes as follows:

(1) Simulate Eqs. (20a)–(20d) with three weak pulses and calculate the polarization according to Eq. (23). We denote this polarization has $\mathcal{P}_{\epsilon_1\epsilon_2\epsilon_3}(t)$. The initial conditions of the trajectories are sampled from $P_0(\bar{\alpha})$ obtained from Eq. (9). The system is initially in its ground state, and we have Eq. (34).

(2) Repeat step 1 three times. Each time, one of the pulses is turned off. This will give $\mathcal{P}_{\epsilon_1\epsilon_20}(t)$, $\mathcal{P}_{\epsilon_10\epsilon_3}(t)$, and $\mathcal{P}_{0\epsilon_2\epsilon_3}(t)$.

(3) Repeat step 1 again, but with only one small amplitude pulse turned on $\mathcal{P}_{\epsilon_100}(t)$, $\mathcal{P}_{0\epsilon_20}(t)$, and $\mathcal{P}_{00\epsilon_3}(t)$.

Note that $\mathcal{P}_{000}(t)=0$ because the systems remains in its ground state in the absence of external fields. Upon completion of this procedure, the third-order response function can be calculated [5]

$$S^{(3)}(t-\tau_3,\tau_3-\tau_2,\tau_2-\tau_1)$$
$$=(\mathcal{P}_{\epsilon_1\epsilon_2\epsilon_3}-\mathcal{P}_{\epsilon_1\epsilon_20}-\mathcal{P}_{\epsilon_10\epsilon_3}-\mathcal{P}_{0\epsilon_2\epsilon_3}+\mathcal{P}_{\epsilon_100}$$
$$+\mathcal{P}_{0\epsilon_20}+\mathcal{P}_{00\epsilon_3}-\mathcal{P}_{000})/\epsilon_1\epsilon_2\epsilon_3, \tag{47}$$

provided the pulse amplitudes are sufficiently small. In order to get the full time dependence of the third-order response function, the time at which the pulses act must be varied, and the above three steps repeated.

In the alternative stability matrix approach, we have to calculate the time evolution of M or $M^{(2)}$ instead of simulating the trajectories in the externally driven system. They can be simulated by integrating the equation of motion for the stability matrix [6]

$$\frac{\partial}{\partial t_2}M_{n_1q_1,n_2q_2}(t_2,t_1)=\sum_{n_3,q_3}\frac{\partial\dot{\alpha}_{n_1,q_1}(t_2)}{\partial\alpha_{n_3,q_3}(t_2)}M_{n_3q_3,n_1q_1}(t_2,t_1), \tag{48}$$

and

$$\frac{\partial}{\partial t_3}M^{(2)}_{n_1q_1,n_2q_2,n_3q_3}(t_3,t_2,t_1)=\sum_{n_3,n_4,q_3,q_4}\frac{\partial^2\dot{\alpha}_{n_1,q_1}(t_3)}{\partial\alpha_{n_4,q_4}(t_3)\,\partial\,\alpha_{n_5,q_5}(t_3)}$$
$$\times M_{n_4q_4,n_2q_2}(t_3,t_2)M_{n_5q_5,n_3q_3}(t_3,t_1). \tag{49}$$

The initial conditions to these two stability matrices can be shown to be

$$M_{n_1q_1,n_2q_2}(t_1,t_1)=\delta_{n_1n_2}\delta_{q_1q_2}, \tag{50}$$

and

$$M^{(2)}_{n_1q_1,n_2q_2,n_3q_3}(t_2,t_2,t_1)=0, \tag{51}$$

for all t_1 and t_2. For harmonic systems ($\kappa=0$), $\partial^2\dot{\alpha}_{n_1q_1}(t_3)/\partial\alpha_{n_4q_4}(t_3)\,\partial\alpha_{n_5q_5}(t_3)=0$ and $\partial\dot{\alpha}_{n_1q_1}(t_2)/\partial\alpha_{n_3q_3}(t_2)$ is constant. This can then be used with the initial conditions on the stability matrices to show that the nonlinear response of linearly driven harmonic oscillators vanishes. This well-known result is often understood in terms of cancellation between Liouville-space pathways. [1,42] The stability matrix approach guarantees this cancellation

to be maintained as long as $\langle \alpha_n(0) \rangle = 0$. When $\kappa \neq 0$, $\partial^2 \dot{\alpha}_{n_1 q_1}(t_3)/\partial \alpha_{n_4 q_4}(t_3)\partial \alpha_{n_5 q_5}(t_3)$ and $\partial \dot{\alpha}_{n_1 q_1}(t_2)/\partial \alpha_{n_3 q_3}(t_2)$ are obtained from the Langevin equations [Eqs. (20a)–(20d)]. The simulation steps are as follows:

(1) Simulate the Langevin equations, Eqs. (20a)–(20d), up to time *t in the absence of field.*

(2) For every desired t_1, calculate $M_{n_1 q_1, n_2 q_2}(t_2, t_1)$ and $M^{(2)}_{n_1 q_1, n_2 q_2, n_3 q_3}(t_3, t_2, t_1)$ using Eqs. (48) and (49), respectively.

(3) Evaluate the products appearing inside the averages in Eqs. (35)–(37) using the calculated values for $\bar{\alpha}(t)$, M, and $M^{(2)}$ for the particular trajectory.

(4) Repeat steps 1–3 and take an ensemble average.

IV. RESPONSE OF A SYSTEM COUPLED TO A BATH

Fluctuations due to the coupling with the environment whose strength depends on temperature cause line broadening in optical spectroscopy. We now generalize our results to include couplings to a bath. We assume a many-body excitonic system linearly coupled to a harmonic bath and described by the Hamiltonian

$$\begin{aligned}\hat{H}(t) = {} & \omega_{nm}\hat{a}_n^\dagger \hat{a}_m + \kappa_{nm,kl}\hat{a}_n^\dagger \hat{a}_m^\dagger \hat{a}_k \hat{a}_l \\ & - \epsilon(t)[\mu_n \hat{a}_n + \mu_n^* \hat{a}_n^\dagger + \mu_n^{(2)} \hat{a}_n^\dagger \hat{a}_n \hat{a}_n + (\mu_n^{(2)})^* \hat{a}_n^\dagger \hat{a}_n^\dagger \hat{a}_n] \\ & + C_{n\gamma}\hat{a}_n^\dagger \hat{b}_\gamma + C_{n\gamma}^* \hat{b}_\gamma^\dagger \hat{a}_n + \Omega_\gamma \hat{b}_\gamma^\dagger \hat{b}_\gamma, \end{aligned} \tag{52}$$

where $\hat{b}_\gamma^\dagger$ ($\hat{b}_\gamma$) create (annihilate) an excitation on the oscillator γ of the bath. The coupling between the system and the harmonic bath is included through the $C_{n\gamma}$ terms, and the bath oscillators frequencies are denoted by Ω_γ. We use Greek subscript for the bath and Roman subscript for the system. We also assume that the system only interacts with the field and this interaction is linear. By following the procedure outlined in Sec. II, the time evolution of the density matrix is calculated from

$$\begin{aligned}\dot{\hat{\rho}}(t) = {} & \int d^2\bar{\alpha} d^2\bar{\beta} \frac{\partial P(\bar{\alpha}, \bar{\beta}, t)}{\partial t} \hat{\Lambda}(\bar{\alpha}, \bar{\beta}) \\ = {} & \int d^2\bar{\alpha} d^2\bar{\beta} P(\bar{\alpha}, \bar{\beta}, t) \Bigg(\tilde{A}_n^x \frac{\partial}{\partial \alpha_n^x} + \tilde{A}_n^y \frac{\partial}{\partial \alpha_n^y} + \tilde{B}_n^x \frac{\partial}{\partial \beta_n^x} + \tilde{B}_n^y \frac{\partial}{\partial \beta_n^y} \\ & + \frac{1}{2}\left[G_{A,nk}^x G_{A,mk}^x \frac{\partial^2}{\partial \alpha_n^x \partial \alpha_m^x} + G_{A,nk}^y G_{A,mk}^y \frac{\partial^2}{\partial \alpha_n^y \partial \alpha_m^y} + 2 G_{A,nk}^y G_{A,mk}^x \frac{\partial^2}{\partial \alpha_n^y \partial \alpha_m^x} \right] \\ & + \frac{1}{2}\left[G_{B,nk}^x G_{B,mk}^x \frac{\partial^2}{\partial \beta_n^x \partial \beta_m^x} + G_{B,nk}^y G_{B,mk}^y \frac{\partial^2}{\partial \beta_n^y \partial \beta_m^y} + 2 G_{B,nk}^y G_{B,mk}^x \frac{\partial^2}{\partial \beta_n^y \partial \beta_m^x} \right] + \tilde{A}_\gamma^x \frac{\partial}{\partial \alpha_\gamma^x} + \tilde{A}_\gamma^y \frac{\partial}{\partial \alpha_\gamma^y} + \tilde{B}_\gamma^x \frac{\partial}{\partial \beta_\gamma^x} + \tilde{B}_\gamma^y \frac{\partial}{\partial \beta_\gamma^y} \Bigg) \hat{\Lambda}(\bar{\alpha}, \bar{\beta}), \end{aligned} \tag{53}$$

where $\bar{\alpha}$ is an array containing all the α_n's, and α_γ's (similarly for $\bar{\beta}$). The new $\tilde{A}$'s and $\tilde{B}$'s are defined by

$$\tilde{A}_n = \tilde{A}_n^x + i\tilde{A}_n^y = A_n - \frac{i}{\hbar} C_{n\gamma m}\alpha_\gamma, \tag{54}$$

$$\tilde{B}_n = \tilde{B}_n^x + i\tilde{B}_n^y = B_n + \frac{i}{\hbar} C_{n\gamma}^* \beta_\gamma, \tag{55}$$

$$\tilde{A}_\gamma = \tilde{A}_\gamma^x + i\tilde{A}_\gamma^y = -\frac{i}{\hbar}(\Omega_\gamma \alpha_\gamma + C_{n\gamma}^* \alpha_n), \tag{56}$$

and

$$\tilde{B}_\gamma = \tilde{B}_\gamma^x + i\tilde{B}_\gamma^y = \frac{i}{\hbar}(\Omega_\gamma \beta_\gamma + C_{n\gamma}\beta_n), \tag{57}$$

where A_n and B_n are given by Eqs. (14) and (15), and there is no summation on the first term of the right-hand side of the last two equations even if the index γ is repeated. Note that the G's are unchanged by the coupling to the bath. They are defined by Eqs. (16) and (17).

The steps described in Sec. II are repeated, and the same Langevin equations for α_n and β_n, Eqs. (20a)–(20d) are obtained, but with $\tilde{A}_n$ and $\tilde{B}_n$ replacing A_n and B_n. The equations of motion for the harmonic bath parameters are purely deterministic as

$$\frac{d\alpha_\gamma}{dt} = -\frac{i}{\hbar}\Omega_\gamma \alpha_\gamma - \frac{i}{\hbar} C_{n\gamma}^* \alpha_n \tag{58a}$$

$$\frac{d\beta_\gamma}{dt} = \frac{i}{\hbar}\Omega_\gamma \beta_\gamma + \frac{i}{\hbar} C_{n\gamma}\beta_n, \tag{58b}$$

where we combined the real and imaginary part of α_γ and β_γ. These equations can be formally solved as

$$\alpha_\gamma(t) = e^{-i\Omega_\gamma t/\hbar}\alpha_\gamma(0) - \frac{i}{\hbar}\int_0^t d\tau e^{-i\Omega_\gamma(t-\tau)/\hbar} C_{n\gamma}^* \alpha_n(\tau) \tag{59a}$$

$$\beta_\gamma(t) = e^{i\Omega_\gamma t/\hbar}\beta_\gamma(0) + \frac{i}{\hbar}\int_0^t d\tau e^{i\Omega_\gamma(t-\tau)/\hbar} C_{n\gamma}\beta_n(\tau). \tag{59b}$$

When these solutions are inserted in the system's Langevin equations, the only remaining bath dependence appears in the frequencies and the initial conditions.

Using Eq. (59), the Langevin equations for the system's parameters become

$$\frac{d\alpha_n}{dt} = A_n + G_{A,nm}\xi_m^\ddagger(t) + f_n^\ddagger(t) - \frac{C_{n\gamma}C_{m\gamma}^*}{\hbar^2}\int_0^t d\tau e^{-i\Omega_\gamma/\hbar(t-\tau)}\alpha_m(\tau) \tag{60a}$$

$$\frac{d\beta_n}{dt} = B_n + G_{B,nm}\eta_m^\ddagger(t) + g_n^\ddagger(t) - \frac{C_{n\gamma}^*C_{m\gamma}}{\hbar^2}\int_0^t d\tau e^{i\Omega_\gamma/\hbar(t-\tau)}\beta_m(\tau). \tag{60b}$$

Eliminating the bath variables in the introduction of two noise variables, $f_n^\ddagger(t)$ and $g_n^\ddagger(t)$,

$$f_n^\ddagger(t) = -\frac{i}{\hbar}C_{n\gamma}e^{-i\Omega_\gamma/\hbar t}\alpha_\gamma(0) \tag{61a}$$

$$g_n^\ddagger(t) = \frac{i}{\hbar}C_{n\gamma}^* e^{i\Omega_\gamma/\hbar t}\beta_\gamma(0). \tag{61b}$$

The two new terms on the right-hand side of Eqs. (60a) and (60b) are identical to the standard fluctuation and dissipation terms obtained in classical Langevin equations for a system in a harmonic bath [43]. In order to specify these two new noise variables, we need the initial bath parameters distribution function. We assume that for $t=0$ the system and the bath are decoupled ($C_{n\gamma}=0$), the system is in the ground state, and the bath is described by a canonical distribution

$$\hat{\rho}(t=0) = \sum_{n_1,n_2,\ldots,n_M=1}^{\infty} e^{-\beta\hbar\Sigma_{\gamma=1}^M\Omega_\gamma(n_\gamma+1/2)} \times|\bar{0},n_1,n_2,\ldots,n_M\rangle\langle\bar{0},n_1,n_2,\ldots,n_M| \tag{62}$$

for M bath oscillators, where $\bar{0}$ means that all system's excitons are in their lowest energy state. In this equation, $\beta=1/(k_BT)$ where k_B is Boltzmann's constant and T is the temperature. Note that this initial distribution is stationary only if the bath and the system are decoupled; an approximation often taken for the initial distribution. This is used with Eq. (9) to obtain the following initial distribution for the coherent state system and bath parameters

$$P(\bar{\alpha},\bar{\beta}) = \frac{1}{(4\pi^2)^{N+M}}\exp\left(-\sum_{\gamma=1}^M\left[\frac{\beta\hbar\Omega_\gamma}{2} + \left|\frac{\alpha_\gamma-\beta_\gamma^*}{2}\right|^2 + (1-e^{-\beta\hbar\Omega_\gamma})\left|\frac{\alpha_\gamma+\beta_\gamma^*}{2}\right|^2\right] - \sum_{n=1}^N\left[\frac{(\alpha_n^x)^2+(\alpha_n^y)^2+(\beta_n^x)^2+(\beta_n^y)^2}{2}\right]\right). \tag{63}$$

In particular, it is easy to show that every initial bath parameters have zero mean and the variances of

$$\langle\alpha_\gamma^x\alpha_\gamma^x\rangle = \langle\alpha_\gamma^y\alpha_\gamma^y\rangle = \langle\beta_\gamma^x\beta_\gamma^x\rangle = \langle\beta_\gamma^y\beta_\gamma^y\rangle = [2-\exp(-\beta\hbar\Omega_\gamma)]/[2-2\exp(-\beta\hbar\Omega_\gamma)],$$

$$\langle\alpha_\gamma^x\beta_\gamma^x\rangle = \exp(-\beta\hbar\Omega_\gamma)/[2-2\exp(-\beta\hbar\Omega_\gamma)] = -\langle\alpha_\gamma^y\beta_\gamma^y\rangle;$$

all other correlations vanish. These relations can then be used to obtain the statistical properties of $f_n^\ddagger(t)$ and $g_n^\ddagger(t)$ which have zero mean and

$$\langle f_n^\ddagger(t)(f_m^\ddagger(t'))^*\rangle = \frac{1}{\hbar^2}C_{n\gamma}C_{m\gamma}^* e^{-i\Omega_\gamma/\hbar(t-t')}\langle\alpha_\gamma^x(0)\alpha_\gamma^x(0) + \alpha_\gamma^y(0)\alpha_\gamma^y(0)\rangle, \tag{64a}$$

$$\langle g_n^\ddagger(t)(g_m^\ddagger(t'))^*\rangle = \frac{1}{\hbar^2}C_{n\gamma}C_{m\gamma}^* e^{i\Omega_\gamma/\hbar(t-t')}\langle\beta_\gamma^x(0)\beta_\gamma^x(0) + \beta_\gamma^y(0)\beta_\gamma^y(0)\rangle, \tag{64b}$$

and

$$\langle f_n^\ddagger(t)g_m^\ddagger(t')\rangle = \frac{1}{\hbar^2}C_{n\gamma}C_{m\gamma}^* e^{-i\Omega_\gamma/\hbar(t-t')}\langle\alpha_\gamma^x(0)\beta_\gamma^x(0) - \alpha_\gamma^y(0)\beta_\gamma^y(0)\rangle. \tag{64c}$$

Note that $f_n^\ddagger(t)$ and $g_n^\ddagger(t)$ are now correlated and this correlation vanishes exponentially as temperature approaches zero (in the fully quantum mechanical regime). This analysis shows that for every exciton in the system, the problem requires the solution of four complex first-order stochastic differential equations with extra noise sources due to the presence of the bath.

In practice, we do not know the $C_{n\gamma}$'s and Ω_γ's. On the other hand, many models for the bath simplify the numerical effort and give accurate line broadening [2]. Here we present one of them. We first assume that each exciton is coupled to its own bath. In other words, all the C's are the same and represent a single coupling for each exciton with it's bath, $C_{n\gamma}=\lambda_n$. In such a case, the memory function, $M(t)$, can be rewritten as

$$\frac{C_{n\gamma}C_{m\gamma}^*}{\hbar^2}\int_0^t d\tau e^{-i\Omega_\gamma/\hbar(t-\tau)}\alpha_m(\tau) = \delta_{nm}\frac{|\lambda_n|^2}{\hbar^2}\int_0^t d\tau M(t-\tau)\alpha_n(\tau), \tag{65}$$

where

$$M(t) = \int d\Omega e^{-i\Omega/\hbar t}\mathcal{G}(\Omega), \tag{66}$$

and $\mathcal{G}(\Omega)$ is the bath density of states. We assumed that the initial conditions on different baths were uncorrelated. We also assumed that all excitons were coupled to baths having the same density of states. A common model for the bath density of states is the Debye model for solids. [44] More recent models for baths can be found in the literatures. [2,43] The extra noise terms can also be expressed in terms of the density of states as

$$f_n^{\ddagger}(t) = -\frac{i}{\hbar}\lambda_n \int d\Omega e^{-i/\hbar\Omega t} \mathrm{f}^{\ddagger}(\Omega), \tag{67}$$

and

$$g_n^{\ddagger}(t) = \frac{i}{\hbar}\lambda_n^* \int d\Omega e^{i/\hbar\Omega t} \mathrm{g}^{\ddagger}(\Omega), \tag{68}$$

where we introduced two new noise variables whose variances are related to the density of states and the temperature as

$$\langle \mathrm{f}^{\ddagger}(\Omega)\mathrm{f}^{\ddagger}(\Omega')^* \rangle = \delta(\Omega - \Omega')\mathcal{G}(\Omega)\frac{2 - e^{-\beta\hbar\Omega}}{1 - e^{-\beta\hbar\Omega}},$$

$$\langle \mathrm{g}^{\ddagger}(\Omega)\mathrm{g}^{\ddagger}(\Omega')^* \rangle = \delta(\Omega - \Omega')\mathcal{G}(\Omega)\frac{2 - e^{-\beta\hbar\Omega}}{1 - e^{-\beta\hbar\Omega}},$$

$$\langle \mathrm{f}^{\ddagger}(\Omega)\mathrm{g}^{\ddagger}(\Omega') \rangle = \delta(\Omega - \Omega')\mathcal{G}(\Omega)\frac{e^{-\beta\hbar\Omega}}{1 - e^{-\beta\hbar\Omega}}. \tag{69}$$

Hence, the extra friction and dissipation terms in Eqs. (50) can be calculated by performing simple integrals over the model bath density of states. This suggests a way to reduce the numerical effort by avoiding sums over all bath degrees of freedom.

V. COMPARISON OF SIMULATION COST

We now compare the numerical effort required to compute the third-order response function using the nonequilibrium and the stability matrix approaches for the model presented in Secs. II and III.

In the nonequilibrium method, the Langevin equations must be simulated with the fields turned on. For N degrees of freedom, the number of multiplications for each time step is proportional to N^4 [see Eqs. (14) and (15) and Eqs. (20a)–(20d)]. Therefore, the time required to compute the average polarization for one specific pulse sequence scales as $N^4 \times N_t \times N_{\mathrm{traj}}$, where N_t is the number of time steps taken in the simulation and N_{traj} is the number of trajectories in the ensemble. Then, the third-order response function can be calculated by varying the time at which the pulses act. If we assume the system to be at equilibrium at time zero, we set $\tau_1 = 0$ and vary τ_2 and τ_3 only. We denote the number of discrete values of τ_2 and τ_3 by N_τ. Increasing N_τ means higher time resolution of the spectra. The total time required to calculate the third-order response function with the nonequilibrium method scales as

$$t_{\mathrm{ne}} \propto N^4 \times N_t \times N_\tau^2 \times N_{\mathrm{traj}}. \tag{70}$$

In the stability matrix approach, the rate-determining step is the calculation of the second order stability matrix $M_{ijk}^{(2)}(t_3, t_2, t_1)$. For each time step, the second order stability matrix requires the integration of N^2 equations of motion [Eq. (49)]. The total computation time required in the stability matrix approach scales as

$$t_{\mathrm{sm}} \propto N^6 \times N_t \times N_{\mathrm{traj}}. \tag{71}$$

The ratio of the two estimated times is given by

$$\frac{t_{\mathrm{sm}}}{t_{\mathrm{ne}}} \propto \frac{N^2}{N_\tau^2}. \tag{72}$$

Inclusion of the environment only slightly increases the number of operations to be done at each time step. The stability matrix approach is $\sim N^2$ more expensive than the nonequilibrium approach because the second order stability matrix requires the integration of the equation of motion for all N^2 deviations of $\dot{\alpha}$ with respect to α. On the other hand, as the time intervals between pulses are varied, new trajectory calculation is required in the nonequilibrium, but not in the stability matrix approach. Thus, higher time resolution increases the computational cost of the nonequilibrium simulation.

VI. CONCLUSIONS

This paper demonstrates how the positive P-representation can be used to compute the nonlinear response functions of a many-body bosonic system driven by impulsive pulses. The response functions can be calculated using a set of classical-like Langevin equations. Therefore, previously developed methodologies for calculating response functions of classical systems [7,12,13] can be directly applied here, and the memory expensive computation of excited states wave functions and energies is avoided.

Each boson degrees of freedom is associated with two complex variables (α and β) in the P-representation, and their resulting equations of motion are complex conjugates. The anharmonicity in the system's Hamiltonian gives rise to coupling between the α and the β variables. There are three sources for the noise in the Langevin equations: anharmonicity of the system's Hamiltonian, nonlinear interaction with the fields, and interactions with the environment.

The P-representation was used to compute the response of the system. In the nonequilibrium approach, weak impulsive temporally well-separated pulses are explicitly kept in the Langevin equations, and the third-order response function can be calculated from Eq. (28c). In the stability matrix approach, small deviations of α and $\dot{\alpha}$ are imposed in the trajectory, and the time evolution of the deviations is simulated. Equations of motion for the stability matrices are obtained just like for their classical analogs. The third-order response function can be calculated following Eq. (36). In the nonequilibrium simulation, the calculation of the stability matrix can be avoided. However, ensemble averages are required when the time intervals are varied. Thus, high time resolution increases the computational cost of the nonequilibrium approach but not of the stability matrix approach. The nonlinear response of linearly driven harmonic systems vanishes identically because of interfering pathways. One clear advantage of the stability matrix approach is that it enforces this cancellation provided that the mean of the initial distribution of α and β vanishes (this is clearly the case when the system is in its ground state).

The similarity of the Langevin equations with their classical counterparts allows us to use standard techniques. Coupling the system with a harmonic bath is included in the Langevin equation as an extra source of noise. It generally

translates into colored noise and memory terms. The decay of the correlation of the noise is governed by the bath temperature and the vibrational density of states of the bath, much like classical systems.

The positive P-representation is not unique [31] and the convergence of the average polarization may require a large number of trajectories. As shown in Fig. 1 of Ref. [40], the number of excitations in a damped 2-bosons systems as predicted by the P-representation can diverge. On the other hand, this nonuniqueness could allow the use of other Gauges like the one proposed in Refs. [31,40,45] to reduce the numerical effort and get convergence. Deuar *et al.* [45] had tested some of these Gauges on a system made of two coupled anharmonic oscillators and a one-dimensional gas of bosons and reported the computational cost required to achieve convergence of relevant statistical quantities (i.e., probability of being in a given state). Only after a numerical implementation of the formalism described in this paper will we be able to say how the response function calculation will be sensitive to the known convergence problems associated with the positive P-representation. The convergence of the response function is strongly dependent on the system. In the future, we plan to implement our formalism on a many-body bosonic system composed of a few number of sites and discuss in depth the computational cost for calculating the response function with the positive P-representation.

Throughout this paper, we treated the field and the transition dipoles as scalars, for simplicity. The formalism can be easily generalizable to include these vector in three dimensions.

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