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Superoperator representation of nonlinear response: Unifying quantum field and mode coupling theories

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Computing response functions by following the time evolution of superoperators in Liouville space (whose vectors are ordinary Hilbert space operators) offers an attractive alternative to the diagrammatic perturbative expansion of many-body equilibrium and nonequilibrium Green's functions. The bookkeeping of time ordering is naturally maintained in real (physical) time, allowing the formulation of Wick's theorem for superoperators, giving a factorization of higher order response functions in terms of two fundamental Green's functions. Backward propagations and analytic continuations using artificial times (Keldysh loops and Matsubara contours) are avoided. A generating functional for nonlinear response functions unifies quantum field theory and the classical mode coupling formalism of nonlinear hydrodynamics and may be used for semiclassical expansions. Classical response functions are obtained without the explicit computation of stability matrices.

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I. INTRODUCTION

An important ingredient in many-body theories is the ability to factorize averages of products of a large number of operators into products of averages of pairs. This Wick theorem is common to the broad arsenal of techniques used for the treatment of quantum and classical systems alike. Quantized fields are used, e.g., in Green's function perturbation theory of many identical bosons or fermions [1–7]; time dependent Hartree-Fock and time dependent density functional equations of motion of many-electron systems [8]; and the Hartree-Fock Bogoliubov equations for superconductors and Bose-Einstein condensates [9]. Classical fields are considered in mode coupling theories of nonlinear hydrodynamics of fluids and glasses [10,11]; cumulant ($1/N$) expansions for short range interactions in fluids; and Gaussian models of spin Hamiltonians [12–18].

Green's function perturbation theory forms the basis for the powerful Feynman diagrammatic techniques widely used in the description of many-particle systems [1–9]. This formalism is based on expressing quantities of interest as *time-ordered expansions*. Equilibrium and nonequilibrium Green's function techniques [5,7,19] employ various types of contours which, in effect, transform the computation to a time-ordered form in some artificial (unphysical) time variable along the contour [20–22].

The primary goal of this article is to demonstrate that the description is greatly simplified by employing superoperator algebra and computing response functions using the density matrix in Liouville space [23–26]. One of the rewards of working in the higher dimensional Liouville space is that we need consider only time-ordered quantities in real (physical) time, and Wick's theorem therefore assumes a particularly compact form; no special contours or analytic continuations are necessary. The Hilbert space description requires a sequence of forward and backward propagations as opposed to the all-forward representation of response functions in Liouville space [27–31]. The superoperator approach provides a unifying framework applicable to quantum and classical systems, with and without second quantization. It thus connects field theories with classical mode coupling theories of fluctuating hydrodynamics. Semiclassical approximations are developed directly for nonlinear response functions (i.e., specific combinations of correlation functions) rather than for individual correlation functions, which do not have a natural classical limit and their semiclassical approximations are thus ill defined. Recent interest in multidimensional Raman techniques generated considerable activity in modeling multitime correlation functions [32–40]. The mode coupling simulation of correlation functions using Langevin equations poses many problems [13,33]. These difficulties disappear by modeling the entire response where the classical limit is uniquely and unambiguously recovered. The present formalism shows how nonlinear response functions may be expressed in terms of the lower order response of collective variables [25,26,41].

In Sec. II we discuss two strategies for simulating response functions. The first, based on the wave function in Hilbert space, does not maintain a full bookkeeping of time ordering whereas the second, based on the density matrix in Liouville space, does [42–44]. A detailed comparison is made of the physical insight and the numerical effort required in both pictures. These results form the basis for developing the many-body Green's function perturbation theory in Sec. III. Using a generalized superoperator generating functional, we obtain a time-ordered perturbation theory of elementary Liouville space operators, and derive Wick's theorem for boson field superoperators in Sec. IV. These results are used in Sec. V to derive a semiclassical expansion for response functions which in the classical limit recovers mode coupling theory. The extension to fermion fields is made in Sec. VI, and our results are summarized and discussed in Sec. VII.

Wick's theorem is based on a perturbative expansion

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around a quadratic Hamiltonian and is thus limited to physical situations when this is a good reference for the actual dynamics. It is given for boson fields in Sec. IV using a closed expression for the generating functional, and for fermion fields in Sec. VI. In Sec. V we explore it in coordinate space without using second quantization. Section II introduces the notation and reviews previous results. The superoperator algebra of Sec. III was used earlier for specific applications (time dependent Hartree-Fock, fifth Raman spectroscopy) [24–26,45]. This section recasts these earlier results in a more general and compact notation that sets the stage for the subsequent sections.

II. LIOUVILLE VS HILBERT SPACE DESCRIPTION OF QUANTUM NONLINEAR RESPONSE

A. Partially time-ordered, wave function based expansion of response functions

We consider a material system with Hamiltonian H, coupled to an external driving field $E(\tau)$ by the interaction

$$H_{int}(\tau)=-AE(\tau), \tag{1}$$

where A is a general dynamical variable. For clarity we assume a scalar field; extension to vector fields is straightforward by introducing tensor notation. The total Hamiltonian $H_T(\tau)$ is given by

$$H_T(\tau)=H+H_{int}(\tau). \tag{2}$$

We shall be interested in the expectation value of an operator B of the driven system at time t. For a system described by a wave function $|\psi_j(t)\rangle$ this is given by $S(t)\equiv\langle\psi_j(t)|B|\psi_j(t)\rangle$. A perturbative calculation of $|\psi_j(t)\rangle$ then gives to nth order in the field

$$S_j^{(n)}(t)=\sum_{m=0}^{n}\langle\psi_j^{(m)}(t)|B|\psi_j^{(n-m)}(t)\rangle. \tag{3}$$

Here $|\psi_j^{(m)}\rangle$ denotes the wave function to mth order in H_{int}. If the system is initially in a mixed state (e.g., a canonical distribution) where the state $|j\rangle$ is occupied with probability P_j, we need to average Eq. (3) over that ensemble:

$$S^{(n)}(t)=\sum_j P_j S_j^{(n)}(t). \tag{4}$$

Time dependent perturbation theory gives for the linear response [23]

$$S_j^{(1)}(t)=\frac{i}{\hbar}\int_{-\infty}^{t}d\tau_1\langle\psi_j|U^\dagger(t-\tau_1)BU(t-\tau_1)A|\psi_j\rangle E(\tau)+\text{c.c.} \tag{5}$$

Here $|\psi_j\rangle\equiv|\psi_j(0)\rangle$ and $U(\tau)$ is the *retarded* evolution operator in Hilbert space which propagates the wave function forward in time:

$$U(\tau)=\theta(\tau)\exp\left(-\frac{i}{\hbar}H\tau\right), \tag{6}$$

whereas the *advanced* Green's function

$$U^\dagger(\tau)=\theta(\tau)\exp\left(\frac{i}{\hbar}H\tau\right) \tag{7}$$

is responsible for backward propagation. $\theta(\tau)$ denotes the Heaviside function (0 for $\tau<0$, 1 for $\tau>0$).

For the third order response, which describes many of the most common nonlinear spectroscopies [23], we obtain

$$S_j^{(3)}(t)=\left(\frac{i}{\hbar}\right)^3\int_{-\infty}^{t}d\tau_1\int_{-\infty}^{t}d\tau_2\int_{-\infty}^{\tau_2}d\tau_3R_a(t,\tau_3,\tau_2,\tau_1)E(\tau_1)E(\tau_2)E(\tau_3)+\left(\frac{i}{\hbar}\right)^3\int_{-\infty}^{t}d\tau_1\int_{-\infty}^{\tau_1}d\tau_2\int_{-\infty}^{\tau_2}d\tau_3R_b(t,\tau_3,\tau_2,\tau_1)E(\tau_1)E(\tau_2)E(\tau_3)+\text{c.c.}, \tag{8}$$

where

$$R_a(\tau_4,\tau_3,\tau_2,\tau_1)=\langle\psi_j|U^\dagger(\tau_{31})AU^\dagger(\tau_{23})AU^\dagger(\tau_{42})BU(\tau_{41})A|\psi_j\rangle,$$

$$R_b(\tau_4,\tau_3,\tau_2,\tau_1)=\langle\psi_j|U^\dagger(\tau_{41})BU(\tau_{43})AU(\tau_{32})AU(\tau_{21})A|\psi_j\rangle, \tag{9}$$

and we have defined $\tau_4\equiv t$ and $\tau_{ij}\equiv\tau_i-\tau_j$. These equations represent a time loop of forward and backward propagations [46]. Equation (9) may alternatively be recast using correlation functions:

$$R_a(\tau_4,\tau_3,\tau_2,\tau_1)=\langle\psi_j|\hat{A}(\tau_3)\hat{A}(\tau_2)\hat{B}(\tau_4)\hat{A}(\tau_1)|\psi_j\rangle,$$

$$R_b(\tau_4,\tau_3,\tau_2,\tau_1)=\langle\psi_j|\hat{B}(\tau_4)\hat{A}(\tau_3)\hat{A}(\tau_2)\hat{A}(\tau_1)|\psi_j\rangle, \tag{10}$$

where we denote operators in the Heisenberg picture by a caret,

$$\hat{A}(\tau) \equiv U^{\dagger}(\tau) A U(\tau). \tag{11}$$

The time variables of R_c in Eq. (8) are fully ordered ($\tau_1 \leqslant \tau_2 \leqslant \tau_3 \leqslant t$). However, this is not the case for R_a and R_b. By breaking the integrations into various segments we can maintain full time ordering, and recast Eq. (8) using a response function. This will be done next through the density matrix expansion.

B. Time-ordered expansion: Response functions

Rather than using a wave function, the state of the system can be described by its density matrix, defined as

$$\rho(t) = \sum_j |\psi_j(t)\rangle P_j \langle \psi_j(t)|. \tag{12}$$

Equations (3) and (4) can alternatively be recast in the form

$$S^{(n)}(t) = \mathrm{Tr}[B\rho^{(n)}(t)], \tag{13}$$

where

$$\rho^{(n)}(t) = \sum_j \sum_{m=0}^{n} P_j |\psi_j^{(m)}(t)\rangle\langle\psi_j^{(n-m)}(t)| \tag{14}$$

is the density matrix expanded to the nth order in H_{int}. The expectation value of B to nth order in the field is obtained by computing the density matrix to the same order. This gives [23]

$$S^{(n)}(t) = \int_{-\infty}^{t} d\tau_n \int_{-\infty}^{\tau_n} d\tau_{n-1} \cdots \int_{-\infty}^{\tau_2} d\tau_1 \times R^{(n)}(t, \tau_n, \tau_{n-1}, \ldots, \tau_1) E(\tau_1) E(\tau_2) \cdots E(\tau_n). \tag{15}$$

Here $R^{(n)}$ is the *nth order response function*

$$R^{(n)}(\tau_{n+1}, \ldots, \tau_1) = \left(\frac{i}{\hbar}\right)^n \mathrm{Tr}\{[\ldots,[[\hat{B}(\tau_{n+1}), \hat{A}(\tau_n)], \hat{A}(\tau_{n-1})], \ldots, \hat{A}(\tau_1)]\rho_{eq}\}, \tag{16}$$

which can alternatively be recast as

$$R^{(n)}(\tau_{n+1}, \ldots, \tau_1) = \left(\frac{i}{\hbar}\right)^n \mathrm{Tr}\{\hat{B}(\tau_{n+1}) \times [\hat{A}(\tau_n), \ldots, [\hat{A}(\tau_2), [\hat{A}(\tau_1), \rho_{eq}]], \ldots]\}. \tag{17}$$

Note that the time variables τ_j in Eq. (8) are not ordered. In contrast, the complete time ordering in Eq. (15) makes the density matrix description most intuitive and directly connected to experiment [23].

In the density matrix formulation we maintain a simultaneous bookkeeping of the interactions with the ket and with the bra. This is why Eq. (17) has 2^n terms, each constituting a distinct *Liouville space pathway*. The wave function calculation, in contrast, focuses on amplitudes and the various time orderings of the ket and the bra interactions are lumped together. Equation (3) thus has only $n+1$ terms. The different terms in this case simply reflect the order of the interactions within the bra and within the ket (but not the relative time ordering of bra and ket interactions). When the system interacts with a thermal bath, the 2^n terms in Eq. (17) represent distinct physical processes and their separate treatment is absolutely crucial. The density matrix separates these terms directly and naturally without the need for any change of time variables.

The quantum nonlinear response function $R^{(n)}$ is given by a combination of $(n+1)$ order correlation functions. Response functions provide a natural link between theory and experiment [47]. $R^{(n)}$ is a purely material quantity which contains all the necessary information for describing the nth order response. It is independent of the details of a particular measurement, (e.g., the temporal sequences of pulses as well as their frequencies and wave vectors). The field envelopes enter through the multitime convolutions in Eq. (15). When $S^{(n)}$ is calculated in terms of the wave function without using response functions [Eq. (4)], we need to repeat the calculation for every new realization of the field. $R^{(n)}$ is therefore a compact and economical way for clarifying the fundamental relationships among various techniques and their information content. Since the nonlinear response functions are successively probing higher order correlation functions, they necessarily carry additional information as the order n is increased.

C. Forward/backward vs all-forward representation of response functions

The expression for the response obtained by expanding the density matrix in powers of the external field [Eq. (16)] separates naturally into several contributions, each representing a distinct time ordering of the various interactions. The time variables appearing in Eq. (15) are chronologically ordered and represent successive interactions with the field. In contrast, the time variables in the wave function description are not fully ordered and consequently have a much less transparent physical interpretation. $R^{(n)}$ has 2^n terms (Liouville space pathways) in the density matrix description [Eq. (16)] but only $n+1$ terms using wave functions [Eq. (8)]. In practice, we need compute only half of the terms since they come in complex conjugate pairs.

For the linear response Eq. (16) gives

$$R^{(1)}(\tau_2, \tau_1) = \frac{i}{\hbar} \sum_j P_j \langle \psi_j | U^{\dagger}(\tau_{21}) B U(\tau_{21}) A | \psi_j \rangle + \text{c.c.} \tag{18}$$

The third order response is similarly given by

$$R^{(3)}(\tau_4,\tau_3,\tau_2,\tau_1)=\left(\frac{i}{\hbar}\right)^3\sum_{s=1}^{4}R_s^{(3)}(\tau_4,\tau_3,\tau_2,\tau_1)+\text{c.c.},\tag{19}$$

$$\begin{aligned}
&R_1^{(3)}(\tau_4,\tau_3,\tau_2,\tau_1)\\
&\quad=\sum_j P_j\langle\psi_j|U^\dagger(\tau_{21})AU^\dagger(\tau_{32})AU^\dagger(\tau_{43})BU(\tau_{41})A|\psi_j\rangle,\\
&R_2^{(3)}(\tau_4,\tau_3,\tau_2,\tau_1)\\
&\quad=\sum_j P_j\langle\psi_j|U(\tau_{21})AU^\dagger(\tau_{31})AU^\dagger(\tau_{43})BU(\tau_{42})A|\psi_j\rangle,\\
&R_3^{(3)}(\tau_4,\tau_3,\tau_2,\tau_1)\\
&\quad=\sum_j P_j\langle\psi_j|U(\tau_{31})AU^\dagger(\tau_{21})AU^\dagger(\tau_{42})BU(\tau_{43})A|\psi_j\rangle,\\
&R_4^{(3)}(\tau_4,\tau_3,\tau_2,\tau_1)\\
&\quad=\sum_j P_j\langle\psi_j|U^\dagger(\tau_{41})BU(\tau_{43})AU(\tau_{32})AU(\tau_{21})A|\psi_j\rangle.
\end{aligned}\tag{20}$$

Unlike Eq. (8), Eq. (15) allows us to define a response function since it is fully time ordered. Note that $R_4=R_b$, and R_a corresponds to $R_1+R_2+R_3$.

Equations (18) and (19) can be calculated by either expanding the correlation functions in eigenstates or using wave packets in the coordinate representation. Semiclassically, it is possible to expand $|\psi_j(t)\rangle$ in coherent states $|\psi_j(t)\rangle=\int\int d\mathbf{p}d\mathbf{q}|\mathbf{pq}\rangle\langle\mathbf{pq}|\psi_j(t)\rangle$. Each R_j may thus be computed as an average given by a sum over trajectories moving forward and backward in time as given by the various U and $U^\dagger$ factors, respectively. Coherent states provide an overcomplete basis set [48]. Powerful semiclassical approximations were developed for carrying out this propagation [27–31,49].

In Eqs. (19) and (20) we used the density matrix to derive formal expressions for the response functions, but for the actual calculation we went back to the wave function in Hilbert space. Since quantum mechanics is usually described in terms of wave functions, wave packet and semiclassical descriptions are normally developed for wave functions. It is possible, however, to construct an alternative forward propagating wave packet picture by staying with the density matrix in Liouville space all the way. To that end we represent the time dependent density matrix as

$$\rho(t)=U(t)\rho(0)U^\dagger(t)\equiv\mathcal{G}(t)\rho(0).\tag{21}$$

The first equality is the common representation where we treat $\rho(t)$ as an *operator in Hilbert space*. In the second equation we consider $\rho(t)$ as a *vector in Liouville space*. We further introduce the Liouville space evolution operator

$$\mathcal{G}(t)=\theta(t)\exp\left(-\frac{i}{\hbar}Lt\right),\tag{22}$$

where $LA\equiv[H,A]$ is the Liouville operator.

We shall denote superoperators by the subscript $\nu=L,R$ where the operators A_L and A_R act on the ket (left) and bra (right) of the density matrix ($A_LB\equiv AB$ and $A_RB\equiv BA$) [50]. We further define the equilibrium distribution function

$$\rho_{eq}=\sum_j P_j|\psi_j(0)\rangle\langle\psi_j(0)|.\tag{23}$$

Adopting this notation for Eq. (17) yields for the linear response

$$R^{(1)}(\tau_2,\tau_1)=\text{Tr}[B_L\mathcal{G}(\tau_{21})A_L\rho_{eq}]+\text{c.c.}\tag{24}$$

and for the third order response

$$\begin{aligned}
&R_1^{(3)}(\tau_4,\tau_3,\tau_2,\tau_1)\\
&\quad=\text{Tr}[B_L\mathcal{G}(\tau_{43})A_R\mathcal{G}(\tau_{32})A_R\mathcal{G}(\tau_{21})A_L\rho_{eq}],\\
&R_2^{(3)}(\tau_4,\tau_3,\tau_2,\tau_1)\\
&\quad=\text{Tr}[B_L\mathcal{G}(\tau_{43})A_R\mathcal{G}(\tau_{32})A_L\mathcal{G}(\tau_{21})A_R\rho_{eq}],\\
&R_3^{(3)}(\tau_4,\tau_3,\tau_2,\tau_1)\\
&\quad=\text{Tr}[B_L\mathcal{G}(\tau_{43})A_L\mathcal{G}(\tau_{32})A_R\mathcal{G}(\tau_{21})A_R\rho_{eq}],\\
&R_4^{(3)}(\tau_4,\tau_3,\tau_2,\tau_1)\\
&\quad=\text{Tr}[B_L\mathcal{G}(\tau_{43})A_L\mathcal{G}(\tau_{32})A_L\mathcal{G}(\tau_{21})A_L\rho_{eq}].
\end{aligned}\tag{25}$$

Note that since the density matrix needs only to be propagated forward, Eqs. (25) contain only the forward propagator $\mathcal{G}(t)$ and not its Hermitian conjugate $\mathcal{G}^\dagger(t)$, which describes backward propagation. This is in contrast with the Hilbert space expression [Eq. (20)], which contains both $U(\tau)$ and $U^\dagger(\tau)$.

As in the wave function picture, the response functions may be computed by sums over states or by semiclassical wave packets:

$$\rho_j^{(n)}(t)=\int\int d\mathbf{p}d\mathbf{q}d\mathbf{p}'d\mathbf{q}'|\mathbf{p}'\mathbf{q}'\rangle\langle\mathbf{p}'\mathbf{q}'|\rho_j^{(n)}(t)|\mathbf{pq}\rangle\langle\mathbf{pq}|.\tag{26}$$

Each term *(Liouville space path)* in Eq. (25) can be recast in the form [23,51]

$$R_j^{(3)}(\tau_4,\tau_3,\tau_2,\tau_1)=\text{Tr}[B_L\rho_j^{(n)}(t)],\tag{27}$$

where $\rho_j^{(n)}(t)$ is the density matrix generating function for path j, which can be computed using two forward moving trajectories representing the simultaneous evolution of the ket and the bra [28,45]. In the wave function representation we act on the ket only. Propagating the bra forward is equivalent to propagating the ket backward. By keeping track of both bra and ket simultaneously we can enjoy the physically appealing all-forward evolution. Since the various Liouville space pathways are complex quantities, they interfere when added. This interference may result in dramatic effects.

A systematic approach for computing the response functions will be developed in the next section.

III. SUPEROPERATOR ALGEBRA AND THE TIME-ORDERED PERTURBATIVE EXPANSION OF RESPONSE FUNCTIONS

In Eqs. (24) and (25) we introduced the indices L and R to denote the action of a superoperator from the left or the right. In the following manipulations, in particular for the sake of developing a semiclassical picture, it will be useful to define their symmetric ($\nu=+$) and antisymmetric ($\nu=-$) combinations [24]

$$A_- \equiv A_L - A_R; \quad A_+ \equiv \frac{1}{2}(A_L + A_R). \tag{28}$$

Recasting these definitions in Hilbert space using ordinary operators, we get $A_+X \equiv \frac{1}{2}(AX+XA)$, $A_-X \equiv AX-XA$, X being an arbitrary operator. Hereafter we shall use Greek indices to denote superoperators A_ν with either $\nu=L,R$ or $\nu=+,-$.

We consider operators that depend parametrically on time. This time dependence can be either in the Heisenberg picture $\hat{A}_\nu(\tau)$ [Eq. (30)] or in the interaction picture $\tilde{A}_\nu(\tau)$ [Eq. (40)]. By introducing a time ordering operator T for superoperators in Liouville space, we can freely commute various operators without worrying about commutations. T takes any product of superoperators and reorders them in ascending times from right to left. More precisely, we define

$$TA_\nu(\tau_1)B_\mu(\tau_2) = \begin{cases} A_\nu(\tau_1)B_\mu(\tau_2), & \tau_2 < \tau_1, \\ B_\mu(\tau_2)A_\nu(\tau_1), & \tau_1 < \tau_2, \\ \dfrac{1}{2}[A_\nu(\tau_1)B_\mu(\tau_1) + B_\mu(\tau_1)A_\nu(\tau_1)], & \tau_2 = \tau_1, \end{cases} \tag{29}$$

where $A_\nu(\tau)$ is either $\hat{A}_\nu(\tau)$ or $\tilde{A}_\nu(\tau)$. T orders all superoperators such that time decreases from left to right: The latest operator appears in the far left, and so forth. This is the natural time ordering which follows chronologically the various interactions with the density matrix [34]. The precise order in which superoperators appear next to a T operator is immaterial since at the end the order will be fixed anyhow by T. For example, T before an exponent means that each term in the Taylor expansion of this exponent should be time ordered.

We next introduce the Heisenberg picture for superoperators, whose time evolution is governed by the Liouville operator

$$\hat{A}_\nu(\tau) \equiv \hat{\mathcal{G}}^\dagger(\tau,0) A_\nu \hat{\mathcal{G}}(\tau,0) \tag{30}$$

with

$$\hat{\mathcal{G}}(\tau_2,\tau_1) = \theta(\tau_2-\tau_1)\exp\left[-\frac{i}{\hbar}L(\tau_2-\tau_1)\right]. \tag{31}$$

Equation (30) is the Liouville space analog of Eq. (11). The expectation value of B,

$$S(t) = \mathrm{Tr}[B\rho(t)], \tag{32}$$

may now be represented in the form

$$S(t) = \left\langle T\hat{B}_+(t)\exp\left[\frac{i}{\hbar}\int_{-\infty}^{t} d\tau E(\tau)\hat{A}_-(\tau)\right]\right\rangle. \tag{33}$$

The operator $\hat{B}_+(t)$ corresponds to the observation time, whereas $\hat{A}_-(\tau_j)$ represent various interactions with the external field at time τ, and $\langle\cdots\rangle$ denotes averaging with respect to the equilibrium density matrix ρ_{eq}:

$$\langle F \rangle \equiv \mathrm{Tr}[F\rho_{eq}]. \tag{34}$$

By expanding the exponent in the right hand side (RHS) of Eq. (33) in powers of $E(\tau)$, we obtain for the response functions

$$R^{(n)}(\tau_{n+1}\cdots\tau_1) \equiv \left(\frac{i}{\hbar}\right)^n \langle \hat{B}_+(\tau_{n+1})\hat{A}_-(\tau_n)\cdots\hat{A}_-(\tau_1)\rangle. \tag{35}$$

Equation (35) is merely a compact notation for Eq. (17). It should be emphasized that all time arguments are fully ordered, $\tau_1 \leqslant \tau_2 \leqslant \cdots \leqslant \tau_{n+1}$. The Liouville space correlation function in the RHS represents a combination of ordinary (Hilbert space) correlation functions.

Equation (35) may be evaluated directly only for simple models. To convert it into a general computational tool we need to develop a perturbation theory for response functions based on time-ordered superoperators. To that end we partition the Hamiltonian into a simple, solvable (usually quadratic) part H_0 and a perturbation V:

$$H = H_0 + V, \tag{36}$$

and introduce the Heisenberg and interaction pictures. We define the Liouville operators $L = L_0 + V_-$ corresponding to Eq. (36) where $L_0 \equiv (H_0)_-$, i.e., $L_0 X \equiv H_0 X - X H_0$. The time evolution operator with respect to L_0 is

$$\mathcal{G}_0(\tau_2,\tau_1) = \theta(\tau_2-\tau_1)\exp\left[-\frac{i}{\hbar}L_0(\tau_2-\tau_1)\right]. \tag{37}$$

The total (Heisenberg) time evolution operator with respect to L will be denoted $\hat{\mathcal{G}}(\tau_2,\tau_1)$. We can then write

$$\hat{\mathcal{G}}(\tau_2,\tau_1) = \mathcal{G}_0(\tau_2,\tau_1)\tilde{\mathcal{G}}(\tau_2,\tau_1), \tag{38}$$

where $\tilde{\mathcal{G}}$ is the time evolution operator in the interaction picture:

$$\tilde{\mathcal{G}}(\tau_2,\tau_1) = T\exp\left[-\frac{i}{\hbar}\int_{\tau_1}^{\tau_2} d\tau_2 \tilde{V}_-(\tau)\right]. \tag{39}$$

Throughout this paper we use a caret to denote operators in the Heisenberg picture [Eq. (30)] and a tilde for operators in the interaction picture, i.e.,

$$\tilde{A}_\nu(\tau)\equiv\mathcal{G}_0^\dagger(\tau,0),A_\nu\mathcal{G}_0(\tau,0), \tag{40}$$

$$\nu=+,- \quad \text{or} \quad L,R.$$

The equilibrium density matrix of the interacting system can be generated from the density matrix of the noninteracting system (ρ_0) by an adiabatic switching of the coupling V, resulting in

$$\rho_{eq}=\tilde{\mathcal{G}}(0,-\infty)\rho_0. \tag{41}$$

For an isolated system at zero temperature, Eq. (41) generates the ground state density matrix of the interacting system, starting with the noninteracting ground state. This is the procedure of Gell-Mann and Low [52]. At zero temperature the zero order ground state evolves into the actual normalized ground state and hence Eq. (41) need not have a denominator. Note that in the wave function (Gell-Mann–Low) formulation of adiabatic switching, the wave function acquires a singular phase which must be canceled by a denominator given by the closed loop S matrix; the Liouville space expression is simpler since the phase never shows up. A remarkable point is that Eq. (41) holds as well at finite temperatures provided the system is coupled to a bath at constant temperature. This is a thermodynamic adiabatic switching where the populations of adiabatic states change and equilibrate with the bath at all times [53–55]. It is distinct from the adiabatic switching of an isolated quantum system where the populations of adiabatic states do not change [56].

At finite temperatures we start with the grand canonical distribution

$$\rho_0=\frac{\exp[-\beta(H_0-\mu N)]}{\mathrm{Tr}\exp[-\beta(H_0-\mu N)]}, \tag{42}$$

where $\beta=(k_BT)^{-1}$ (k_B is the Boltzmann constant), μ is the chemical potential, N is the number operator of particles, and Eq. (41) generates the distribution

$$\rho_{eq}=\frac{\exp[-\beta(H-\mu N)]}{\mathrm{Tr}\exp[-\beta(H-\mu N)]}. \tag{43}$$

We now have all the ingredients required for computing the response. Let us start with the linear response function

$$R^{(1)}(\tau_2,\tau_1)=\frac{i}{\hbar}\langle\hat{B}_+(\tau_2)\hat{A}_-(\tau_1)\rangle. \tag{44}$$

Using Eqs. (30) and (38) we obtain

$$R^{(1)}(\tau_2,\tau_1)=\frac{i}{\hbar}\mathrm{Tr}[\tilde{\mathcal{G}}^\dagger(\tau_2,0)\tilde{B}_+(\tau_2)\tilde{\mathcal{G}}(\tau_2,0)\tilde{\mathcal{G}}^\dagger(\tau_1,0)$$
$$\times\tilde{A}_-(\tau_1)\tilde{\mathcal{G}}(\tau_1,0)\tilde{\mathcal{G}}(0,-\infty)\rho_0]. \tag{45}$$

The last $\tilde{\mathcal{G}}^\dagger(\tau_2,0)$ can be neglected since it does not affect the trace. Also

$$\tilde{\mathcal{G}}(\tau_2,0)\tilde{\mathcal{G}}^\dagger(\tau_1,0)=\tilde{\mathcal{G}}(\tau_2,\tau_1), \tag{46}$$

which gives

$$R^{(1)}(\tau_2,\tau_1)=\frac{i}{\hbar}\ \mathrm{Tr}[\tilde{B}_+(\tau_2)\tilde{\mathcal{G}}(\tau_2,\tau_1)\tilde{A}_-(\tau_1)\tilde{\mathcal{G}}(\tau_1,-\infty)\rho_0]. \tag{47}$$

The time-ordering operator allows us to express Eq. (47) in the compact form

$$R^{(1)}(\tau_2,\tau_1)=\frac{i}{\hbar}\left\langle T\tilde{B}_+(\tau_2)\tilde{A}_-(\tau_1)\right.$$
$$\left.\times\exp\left[-\frac{i}{\hbar}\int_{-\infty}^{\tau_2}d\tau\tilde{V}_-(\tau)\right]\right\rangle_0, \tag{48}$$

where we define averaging with respect to the density matrix ρ_0 of the noninteracting system

$$\langle F\rangle_0\equiv\ \mathrm{Tr}[F\rho_0]. \tag{49}$$

Equation (48) can be immediately generalized for the response to arbitrary order:

$$S(t)=\left\langle T\tilde{B}_+(t)\exp\left[-\frac{i}{\hbar}\int_{-\infty}^{t}d\tau\tilde{V}_-(\tau)\right]\right.$$
$$\left.\times\exp\left[\frac{i}{\hbar}\int_{-\infty}^{t}d\tau E(\tau)\tilde{A}_-(\tau)\right]\right\rangle_0. \tag{50}$$

Expanding Eq. (50) to nth order in the external field gives

$$R^{(n)}(\tau_{n+1}\cdots\tau_1)=\left(\frac{i}{\hbar}\right)^n\left\langle T\tilde{B}_+(\tau_{n+1})\tilde{A}_-(\tau_n)\cdots\tilde{A}_-(\tau_1)\right.$$
$$\left.\times\exp\left[-\frac{i}{\hbar}\int_{-\infty}^{\tau_{n+1}}d\tau\tilde{V}_-(\tau)\right]\right\rangle_0, \tag{51}$$

where we recall that

$$\tilde{X}(\tau)=\exp\left(\frac{i}{\hbar}L_0\tau\right)X\exp\left(-\frac{i}{\hbar}L_0\tau\right), \tag{52}$$

$$X=A_+,A_-,V_-.$$

The Taylor expansion of the exponent in the RHS of Eq. (51) finally gives

$$R^{(n)}(\tau_{n+1}\cdots\tau_1)$$
$$=\sum_{m=0}^{\infty}\frac{(-1)^m}{m!}\left(\frac{i}{\hbar}\right)^{m+n}$$
$$\times\int_{-\infty}^{\tau_{n+1}}d\tau_1'\ldots\int_{-\infty}^{\tau_{n+1}}d\tau_m'\langle T\tilde{B}_+(\tau_{n+1})$$
$$\times\tilde{A}_-(\tau_n)\cdots\tilde{A}_-(\tau_1)\tilde{V}_-(\tau_m')\cdots\tilde{V}_-(\tau_1')\rangle_0. \tag{53}$$

Equation (53) constitutes the interaction-picture representation of the correlation function Eq. (35) [24,41]. All superoperators in this expression should be time ordered chronologically from right (early time) to left (late time). This forms the basis for formulating the field theory and Wick theorem in Liouville space in the next section.

Note that simple time ordering in Liouville space is a more complex operation when recast in Hilbert space. This is why superoperators simplify the bookkeeping. To demonstrate that, let us take $R^{(2)}$ (we use the Heisenberg picture but the argument holds as well in the interaction picture, where we should simply replace all carets by tildes):

$$R^{(2)}(\tau_3,\tau_2,\tau_1)=\left(\frac{i}{\hbar}\right)^2\langle T\hat{B}_+(\tau_3)\hat{A}_-(\tau_2)\hat{A}_-(\tau_1)\rangle_0. \tag{54}$$

We need to apply the superoperators in a time-ordered fashion (in Liouville space), i.e., first $\hat{A}_-(\tau_1)$, then $\hat{A}_-(\tau_2)$, and finally $\hat{B}_+(\tau_3)$. Separating all possible actions for the left and the right we get

$$\begin{aligned}2\ \mathrm{Tr}[T\hat{B}_+(\tau_3)\hat{A}_-(\tau_2)\hat{A}_-(\tau_1)\rho_{eq}]= {}&\mathrm{Tr}[\hat{B}(\tau_3)\hat{A}(\tau_2)\hat{A}(\tau_1)\rho_{eq}]+\mathrm{Tr}[\hat{A}(\tau_2)\hat{A}(\tau_1)\rho_{eq}\hat{B}(\tau_3)]-\mathrm{Tr}[\hat{B}(\tau_3)\hat{A}(\tau_2)\rho_{eq}\hat{A}(\tau_1)]\\&-\mathrm{Tr}[\hat{A}(\tau_2)\rho_{eq}\hat{A}(\tau_1)\hat{B}(\tau_3)]-\mathrm{Tr}[\hat{B}(\tau_3)\hat{A}(\tau_1)\rho_{eq}\hat{A}(\tau_2)]-\mathrm{Tr}[\hat{A}(\tau_1)\rho_{eq}\hat{A}(\tau_2)\hat{B}(\tau_3)]\\&+\mathrm{Tr}[\hat{B}(\tau_3)\rho_{eq}\hat{A}(\tau_1)\hat{A}(\tau_2)]+\mathrm{Tr}[\rho_{eq}\hat{A}(\tau_1)\hat{A}(\tau_2)\hat{B}(\tau_3)].\end{aligned} \tag{55}$$

In Hilbert space [the RHS of Eq. (55)] all operators that act on ρ_{eq} from the left are time ordered and the time increases as we go to the left, starting with ρ_{eq}. All right operators are ordered in the opposite way: Time increases as we go to the right, starting with ρ_{eq}. This mixture of positive and negative time ordering coming from the evolution of the ket (left) and the bra (right), respectively, is what complicates the bookkeeping of ordinary operators in Hilbert space. This is in marked contrast with Liouville space [the LHS of Eq. (55)], where we keep track of the left and right labels of the various interactions. Consequently, all superoperators are always positively time ordered in real, physical time, which makes the formulation of a Wick theorem possible.

IV. THE CUMULANT EXPANSION AND WICK'S THEOREM FOR BOSON SUPEROPERATORS

So far we have considered four types of operators that enter Eq. (51): the reference Hamiltonian $H_0-\mu N$; A, representing the coupling to the external field; V, representing the part of the Hamiltonian to be treated perturbatively; and the desired observable B. To proceed further we introduce the concept of *elementary operators*. Any dynamical system can ultimately be described by a basic set of operators whose commutators (or anticommutators) are c numbers. Examples of elementary operators with commuting algebra (ECA) are the canonical variables $[Q_\alpha,P_\beta]=i\hbar\,\delta_{\alpha\beta}$ and the boson operators $[a_\alpha,a_\beta^\dagger]=\delta_{\alpha\beta}$ used to describe systems of identical bosons in second quantization. Second quantized fermions are described by elementary operators with anticommuting algebra $\{c_\alpha,c_\beta^\dagger\}=\delta_{\alpha\beta}$. The operators $X=A$, B, V, H_0, and N are some functions of these elementary operators.

We choose our reference to be a quadratic Hamiltonian given by the bilinear combination of elementary field operators

$$H_0=\int dx T(x)\psi^\dagger(x)\psi(x), \tag{56}$$

or using creation and annihilation operators

$$H_0=\sum_{r,s} T_{rs}a_r^\dagger a_s, \tag{57}$$

where

$$\psi(x)=\sum_s \varphi_s(x)a_s \tag{58}$$

and φ_s is the single particle basis set. For bosons, these operators satisfy the commutation relations

$$[a_s,a_r^\dagger]=\delta_{rs} \tag{59}$$

and

$$[\psi(x),\psi^\dagger(x')]=\delta(x-x'). \tag{60}$$

For fermions, Eq. (59) should be replaced by an anticommutator. Our elementary set of operators is thus the set $a_s,a_s^\dagger$ or the field operators $\psi(x),\psi^\dagger(x)$. The following arguments hold for fermions as well; however, the derivation is simpler for boson fields with ECA. We shall therefore focus on bosons first, and the extension to fermion fields will be presented in Sec. VI.

We will denote the elementary operators as Q_j and introduce the corresponding superoperators $Q_{j\nu}$, $\nu=L,R,+,-$. We first note that the superoperator corresponding to any function of Q_j can be expressed in terms of Q_{j+} and Q_{j-}, i.e.,

$$\begin{aligned}[f(Q_j)]_-\equiv f(Q_{jL})-f(Q_{jR})={}&f\left(Q_{j+}+\frac{1}{2}Q_{j-}\right)\\&-f\left(Q_{j+}-\frac{1}{2}Q_{j-}\right)\end{aligned} \tag{61}$$

and

$$2[f(Q_j)]_+ \equiv f(Q_{jL}) + f(Q_{jR}) = f\left(Q_{j+} + \frac{1}{2}Q_{j-}\right) + f\left(Q_{j+} - \frac{1}{2}Q_{j-}\right). \tag{62}$$

For example,

$$(Q_j^2)_+ = Q_{j+}^2 + \frac{1}{4}Q_{j-}^2 \tag{63}$$

and

$$(Q_j^2)_- = Q_{j+}Q_{j-} + Q_{j-}Q_{j+}. \tag{64}$$

Using these rules (and additional useful relations given in the Appendix) we can expand $B_+(\tau)$, $A_-(\tau)$, and $V_-(\tau)$ in a Taylor series in Q_{j+} and Q_{j-}, converting the time-ordered product of superoperators in Eq. (53) into a time-ordered product of elementary operators. We thus need to calculate

$$W\{j_m \nu_m \tau_m\} \equiv \langle T\tilde{Q}_{j_N \nu_N}(\tau_N) \cdots \tilde{Q}_{j_1 \nu_1}(\tau_1)\rangle_0, \tag{65}$$

where $\nu_1, \ldots, \nu_N = \pm$ and j_m runs over the various operators. The number N of operators in such products that enter the computation of $R^{(n)}$ is greater than $n+1, N \geqslant n+1$. The reasons are as follows. (i) A_ν, B_ν may be nonlinear functions of elementary operators and we use Eq. (61) and the formulas of the Appendix to express them as products of Q_ν. (ii) The expansion in V_- adds more operators to the product.

To compute W we define a *superoperator generating functional*

$$S[\{J(t)\}] = \left\langle T \exp\left[\sum_{j\nu} \int J_{j\nu}(\tau)\tilde{Q}_{j\nu}(\tau)d\tau\right]\right\rangle_0. \tag{66}$$

Time-ordered correlation functions of superoperators can be obtained from the generating functional by functional derivatives:

$$W\{j_m \nu_m \tau_m\} = \frac{\partial}{\partial J_{j_1\nu_1}(\tau_1)} \cdots \frac{\partial}{\partial J_{j_N\nu_N}(\tau_N)} S\{J(t)\}\Bigg|_{J=0}. \tag{67}$$

Since the Hamiltonian is quadratic, the generating functional may be computed exactly using the second order cumulant expansion. This gives

$$\begin{aligned} S[\{J(t)\}] = \exp\Bigg\{\sum_{j,k} \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\tau_2} d\tau_1 &\times [-i\hbar J_{j+}(\tau_2)J_{k-}(\tau_1)G_{jk}^{+-}(\tau_2-\tau_1) \\ &+ J_{j+}(\tau_2)J_{k+}(\tau_1)G_{jk}^{++}(\tau_2-\tau_1)]\Bigg\}, \end{aligned} \tag{68}$$

where we have introduced the two fundamental Liouville space Green's functions

$$G_{jk}^{+-}(\tau_2-\tau_1) = \frac{i}{\hbar}\langle T\tilde{Q}_{j+}(\tau_2)\tilde{Q}_{k-}(\tau_1)\rangle_0, \tag{69}$$

$$G_{jk}^{++}(\tau_2-\tau_1) = \langle T\tilde{Q}_{j+}(\tau_2)\tilde{Q}_{k+}(\tau_1)\rangle_0.$$

Using Eq. (28) we can recast these Green's functions in Hilbert space as

$$G_{jk}^{+-}(\tau) = \frac{i}{\hbar}\theta(\tau)[\langle\tilde{Q}_j(\tau)\tilde{Q}_k(0)\rangle_0 - \langle\tilde{Q}_j(0)\tilde{Q}_k(\tau)\rangle_0], \tag{70}$$

$$G_{jk}^{++}(\tau) = \frac{1}{2}[\langle\tilde{Q}_j(\tau)\tilde{Q}_k(0)\rangle_0 + \langle\tilde{Q}_k(0)\tilde{Q}_j(\tau)\rangle_0]. \tag{71}$$

The $\hbar^{-1}$ factor in G^{+-} was introduced to make the classical limit more transparent (see the next section), since with this factor G^{+-} has a well defined classical limit. Note that since the trace of a commutator vanishes identically, in a time-ordered product the superoperator to the far left must be a "$+$." The Green's functions G^{--} and G^{-+} thus vanish identically and we only have two fundamental Green's functions G^{++} and G^{+-}. Note also that $G^{++}(\tau)$ is finite for positive and negative τ whereas $G^{+-}(\tau)$ vanishes for $\tau < 0$. Equation (68) is an extremely compact expression which can readily be used to compute response functions to arbitrary order.

The two fundamental Green's functions can be expressed in terms of the matrix of spectral densities $C_{ij}(\omega)$ defined as the Fourier transform of G^{+-} [23,41,57,58]:

$$G_{ij}^{+-}(\tau) = 2\theta(\tau)\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}C_{ij}(\omega)\sin(\omega\tau). \tag{72}$$

We then have

$$G_{ij}^{++}(\tau) = \hbar\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}C_{ij}(\omega)\coth\left(\frac{\hbar\omega}{2k_BT}\right)\cos(\omega\tau). \tag{73}$$

The Wick theorem for superoperators then follows from Eqs. (67) and (68) and can now be stated as follows:

$$\begin{aligned} &\langle T\tilde{Q}_{j_1\nu_1}(\tau_1)\cdots\tilde{Q}_{j_N\nu_N}(\tau_N)\rangle_0 \\ &\quad = \sum_p \langle T\tilde{Q}_{j_a\nu_a}(\tau_a)\tilde{Q}_{j_b\nu_b}(\tau_b)\rangle_0 \cdots \langle T\tilde{Q}_{j_p\nu_p}(\tau_p) \\ &\quad\quad \times \tilde{Q}_{j_q\nu_q}(\tau_q)\rangle_0. \end{aligned} \tag{74}$$

Here $j_a\nu_a \cdots j_q\nu_q$ is a permutation of $j_1\nu_1 \cdots j_N\nu_N$ and the sum runs over all possible permutations, keeping the time ordering. Since only G^{++} and G^{+-} survive, many of the terms will vanish.

Wick's theorem makes it possible to develop Feynman diagram perturbative techniques which express the linear and nonlinear responses of the interacting system in terms of the two fundamental Green's functions. This theorem is useful whenever a quadratic reference is adequate and nonquadratic parts of the Hamiltonian can be treated perturbatively. It states that multipoint correlation functions of systems with quadratic boson Hamiltonians may be factorized into products of two-point correlation functions of the primary coordinates.

V. MODE COUPLING AND SEMICLASSICAL RESPONSE OF BOSON FIELDS

Equation (17) contains 2^n terms representing all possible "left" and "right" actions of the various commutators. Each term corresponds to a Liouville space path and can be represented by a double-sided Feynman diagram [23]. The various correlation functions interfere and this gives rise to many interesting effects such as new resonances. The $(i/\hbar)^n$ factor indicates that individual correlation functions do not have an obvious classical limit. The entire response function must, however, have a classical limit. When the various correlation functions are combined, the $(i/\hbar)^n$ factor is canceled as $\hbar$ tends to 0, and one obtains the classical response, independent of $\hbar$. The elimination of $\hbar$ for higher nonlinearities requires a delicate interference among all 2^n correlation functions.

The terms contributing to $R^{(n)}$ [Eq. (53)] will generally have a $(i/\hbar)^{n+p}$ factor where p is the order in V_-. This factor must be canceled as $\hbar \to 0$ to ensure a well defined classical limit. This is guaranteed since by Wick's theorem we will have $n+p$ G^{+-} terms, each carrying an $\hbar$ factor. In the classical limit we set $\coth(\hbar\omega/2k_BT) \cong 2k_BT/\hbar\omega$. We then see from Eq. (72) that the two Green's functions are simply connected by the classical fluctuation relation

$$G^{+-}(\tau) = -\theta(\tau)\frac{1}{k_BT}\frac{d}{d\tau}G^{++}(\tau). \qquad (75)$$

G^{+-} is independent of $\hbar$. The factor $\hbar\coth(\hbar\omega/2k_BT) = \hbar/\tanh(\hbar\omega/2k_BT)$ is analytic in $\hbar$ and can be expanded in a Taylor series, thus yielding a semiclassical expansion of the response. To obtain the classical limit we need to keep $\hbar$ in the generating functional, perform the $\hbar$ expansion (since response functions are generally analytic in $\hbar$) and only then send $\hbar \to 0$. Setting this limit at the right step is essential for developing a proper semiclassical expansion. Classical response functions may not be computed using classical trajectories alone: The response depends on the vicinity of a trajectory. One needs to run a few closely lying trajectories that interfere. Formally, this can be recast using stability matrices, which carry the information on how a perturbation of a trajectory at a given time affects it at a later time. The repeated computation of the stability matrix greatly complicates purely classical simulations [34,37]. The semiclassical expansion circumvents these calculations in a very profound way. Corrections to the trajectory to low order in $\hbar$ carry the necessary information. Combining several semiclassical trajectories [45] allows them to interfere and the leading order in $\hbar$ ($\hbar^n$ for R^n) survives and gives the classical response. This allows us to avoid computing stability matrices, which is required when the classical limit is considered from the outset. The classical limit obtained in this way reproduces the results of mode coupling theory and removes all ambiguities as to how higher order correlation functions should be factorized [13,17,18,33].

To illustrate how this works, let us consider the following model Hamiltonian H_m [25,26,41,57,59]:

$$H_m = \sum_j \left(\frac{P_j^2}{2M_j} + \frac{M_j\Omega_j^2Q_j^2}{2}\right) + V(\mathbf{Q}), \qquad (76)$$

where $P_j(Q_j)$ is the momentum (coordinate) operator of the jth primary mode, Ω_j and M_j are its frequency and reduced mass, respectively, and $V(\mathbf{Q})$ is the anharmonic part of the potential. The primary modes interact with a large number of harmonic (bath) coordinates which induce relaxation and dephasing. Low frequency bath degrees of freedom $\mathbf{q}$ and their coupling to the primary modes are described by the Hamiltonian H_B, and the material Hamiltonian is given by [23,26]

$$H = H_m(\mathbf{Q}) + H_B(\mathbf{Q},\mathbf{q}). \qquad (77)$$

We assume a harmonic bath linearly coupled to the primary coordinates Q_j,

$$H_B = \sum_\alpha \left[\frac{p_\alpha^2}{2m_\alpha} + \frac{m_\alpha\omega_\alpha^2}{2}\left(q_\alpha - \sum_j \frac{c_{j\alpha}}{m_\alpha\omega_\alpha^2}Q_j\right)^2\right], \qquad (78)$$

where p_α (q_α) are the momentum (coordinate) operators of the bath oscillators.

This model gives the following Brownian oscillator form for the spectral density [57]:

$$C(\omega) = \mathrm{Im}\left(\frac{1}{M[\Omega^2 + \omega\Sigma(\omega) - I\omega^2 + i\omega\gamma(\omega)]}\right). \qquad (79)$$

M, Ω, and E are diagonal matrices and their matrix elements are $M_{ij} = \delta_{ij}M_j$, $\Omega_{ij} = \delta_{ij}\Omega_j$, and $I_{ij} = \delta_{ij}$.

γ_{ij} (Σ_{ij}) is the imaginary (real) part of the self-energy operator representing relaxation (level shift):

$$\gamma_{ij}(\omega) = \frac{\pi}{M_i}\sum_\alpha \frac{c_{j\alpha}c_{i\alpha}}{2m_\alpha\omega_\alpha^2}[\delta(\omega-\omega_\alpha) + \delta(\omega+\omega_\alpha)],$$

$$\Sigma_{ij}(\omega) = -\frac{1}{\pi}\mathrm{Re}\int_{-\infty}^{\infty} d\omega' \frac{\gamma_{ij}(\omega')}{\omega'-\omega}. \qquad (80)$$

Equations (68) and (67), together with Eqs. (72), (73), and (79), constitute closed expressions for the Brownian oscillator response functions. Ordinary Langevin equations are obtained by taking the overdamped limit $\gamma \gg \Omega$ of Eq (79). When the primary coordinates are uncorrelated, the superoperator Green's functions are

$$G_{ij}^{+-}(\tau) = 2\theta(\tau)\exp(-\Lambda_i\tau)\Lambda_i\lambda_i\delta_{ij}, \qquad (81)$$

$$G_{ij}^{++}(\tau)=\hbar\exp(-\Lambda_i\tau)\Lambda_i\lambda_i\coth(\beta\hbar\Lambda_i)\delta_{ij}+\frac{4}{\beta}\sum_{n=1}^{\infty}\frac{\nu_n\exp(-\nu_n\tau)}{\nu_n^2-\Lambda_i^2}\Lambda_i\lambda_i\delta_{ij}, \tag{82}$$

where $\nu_n\equiv 2\pi n/\hbar\beta$ are the Matsubara frequencies, $\Lambda_i=\Omega_i^2/\gamma_{ii}$, and $\lambda_i=1/M_i\Omega_i^2$. The expansion of nonlinear response functions using collective coordinates has been discussed in detail in [23,41,45,60] and recently employed in mode coupling theory [13,15].

All nonlinear response functions of the linearly driven harmonic oscillator vanish identically due to interference among Liouville space paths [23]. The simplest model that shows a finite nonlinear response is a nonlinearly driven harmonic oscillator where the operator A is a nonlinear function of the coordinate. This model has been studied both quantum mechanically and classically [38]. Its response can alternatively be computed by following the dynamics of the Gaussian wave packets in the complete (system and bath) phase space, since the system-bath Hamiltonian H_B is harmonic in the full phase space $\{P,Q,p_\alpha,q_\alpha\}$ [12,13,32,33,61].

We next discuss the connection between our results and a fully classical computation of the response. In classical mechanics the density matrix assumes the form of an ordinary distribution function in phase space. This can be obtained from the quantum density matrix by switching to the Wigner representation [62]

$$\rho_{\mathrm{W}}(\mathbf{pq};t)=\frac{1}{(2\pi\hbar)^d}\int d\mathbf{s}\langle\mathbf{q}-\mathbf{s}/2|\rho(t)|\mathbf{q}+\mathbf{s}/2\rangle\exp(i\mathbf{p}\cdot\mathbf{s}), \tag{83}$$

where d is the number of degrees of freedom. The Wigner representation offers a transparent and simple semiclassical picture that interpolates between the quantum and classical regimes. Wave functions, on the other hand, do not have a clear classical counterpart (although there are, of course, very powerful semiclassical approximations for the wave function such as the WKB approximation).

Wick's theorem for superoperators in Liouville space allows us to develop a unified picture of quantum field and classical mode coupling theories, which clearly reveals the information content of the classical and quantum nonlinear response functions. Both classical and quantum response functions contain interference. Quantum mechanically it is between 2^n Liouville space paths. The classical interference is of a very different nature [63] and involves 2^n close-lying trajectories. The response function in phase space is obtained by ensemble averaging over such bundles of trajectories [45,63]. Alternatively, the classical response can be recast using stability matrices, which carry the relevant dynamical information on the vicinity of a given trajectory. The connection between the quantum and classical 2^n-fold interference is made more transparent by keeping the left/right or the $+/-$ pathways rather than working in phase space. We retain $\hbar$ during the semiclassical calculation and send it to zero only at the end.

In the fully classical phase space approach, we take the two separate (left and right) paths required in a quantum mechanical formalism and expand them around a single classical reference path, letting the stability matrices carry the burden of retaining the information about the differences between the paths. In the present $+/-$ representation we keep track of closely lying trajectories by retaining terms to order $\hbar$ and combine them only at the very end. In this way, stability matrices, which pose enormous computational difficulties [64], never show up.

Another way to view the classical-quantum connection is by starting with the expressions for quantum mechanical nonlinear response functions in terms of combinations of n-point correlation functions of the relevant variables. These correlation functions differ in their time ordering, i.e., $\langle A(\tau_1)A(\tau_2)A(\tau_3)\rangle$, $\langle A(\tau_2)A(\tau_1)A(\tau_3)\rangle$, etc. $R^{(n)}$ is then a combination of 2^n such correlation functions, each representing a distinct Liouville space pathway. Classically, of course, time ordering is immaterial since all operators commute and we have only a single n-point correlation function. The presence (absence) of symmetry with respect to the permutation of the n time variables in classical (quantum) correlation functions implies that the effective multidimensional space of time is reduced by a factor of $n!$ in the classical case. Classical correlation functions thus carry less information than their quantum counterparts. Classically, it suffices to calculate $\langle A(\tau_1)A(\tau_2)\cdots A(\tau_n)\rangle$ for $\tau_1\leqslant\tau_2\leqslant\cdots\leqslant\tau_n$. Quantum mechanically, each of the $n!$ permutations of the time arguments is distinct and carries additional information. The stability matrices provide the extra information required for computing the response functions from classical correlation functions.

Since classical correlation functions do not carry enough information for computing nonlinear response functions, it is not possible to simulate and interpret the response in terms of standard equilibrium fluctuations; additional nonequilibrium information is necessary [63].

Correlation functions are equilibrium objects that can be computed using sums over unperturbed trajectories; response functions can either be obtained as equilibrium averages (stability matrices) or recast in terms of 2^n close-lying nonequilibrium trajectories perturbed at various points in time. Quantum corrections to classical response functions may be represented in terms of classical response functions of higher orders [45].

Finally, we note that an alternative semiclassical $\hbar$ expansion of the response is possible even when the temperature is low compared with the material frequencies, and the system is highly quantum, provided the anharmonicities are weak [24,25]. The leading terms in the expansion can be obtained by solving classical equations of motion. This is done by hiding the $\hbar$ in the coth factor in Eq. (72) by recasting it in the form $\coth(\omega/2\omega_T)$, where $\omega_T=k_BT/\hbar$ is the thermal frequency, and redefining G^{++} by multiplying it by $\hbar$. The response is then analytic in $\hbar$ (as long as we forget about the $\hbar$ dependence of ω_T). Semiclassical approximations ordinarily hold when the temperature is high compared to all relevant vibrational frequencies. This points to a much less obvious, low temperature weak anharmonicity regime, where the response of the system is almost classical even though its temperature is very low.

VI. WICK'S THEOREM FOR FERMION SUPEROPERATORS

One reason that the handling of boson operators and fields is simpler compared to fermions is that superoperators corresponding to elementary boson operators are also elementary, i.e., their commutators are also numbers. To see that, let us consider the commutation rules of superoperators by acting with commutators on an arbitrary operator F:

$$[Q_{jL},Q_{kL}]F=[Q_j,Q_k]F,$$

$$[Q_{jR},Q_{kR}]F=-F[Q_j,Q_k],$$

$$[Q_{jL},Q_{kR}]=0. \tag{84}$$

Since $[Q_j,Q_k]$ is a number, we see that the corresponding superoperators are elementary as well. This property holds also if we consider the linear combinations in the $+,-$ representation. To see that, we start with $[A_+,B_-]$ and act on an ordinary operator F:

$$[A_+,B_-]F=\frac{1}{2}[A,B]F+\frac{1}{2}F[A,B],$$

$$[A_-,B_-]F=4[A_+,B_+]F=[[A,B],F]. \tag{85}$$

Since the commutator of elementary operators is a number, Eq. (85) gives

$$[A_+,B_-]=[A,B],$$

$$[A_-,B_-]=4[A_+,B_+]=0. \tag{86}$$

The commutators of elementary boson superoperators are thus numbers. It then follows that the superoperators corresponding to elementary boson operators are Gaussian, be it in the $+$, $-$ or in the L,R representation. The indices ν in Eq. (74) can thus run over $+$, $-$ or L,R and Wick's theorem holds in either case.

Using L,R, the functional can be used to generate individual Liouville pathways. Using $+,-$ it generates combinations of such paths, making the classical limit more transparent, since we work with combinations of Hilbert space correlation functions which enter the response and have well defined classical limits.

Life is more complicated for fermions. To see that, let us consider the anticommutation rules for Fermi elementary superoperators:

$$\{Q_{jL},Q_{kL}\}F=\{Q_j,Q_k\}F,$$

$$\{Q_{jR},Q_{kR}\}F=F\{Q_j,Q_k\},$$

$$\{Q_{jL},Q_{kR}\}F=2Q_jFQ_k. \tag{87}$$

Since $\{Q_j,Q_k\}$ is a number this shows that left/right or right/left superoperators have elementary anticommutators but the anticommutator of left/right operators is not generally a number. We thus do not have Gaussian statistics. Note, however, that left and right operators always commute. The generating functional needs to be formulated using the Grassman algebra of anticommuting numbers, similar to standard Green's functions [1,6]. The important point is that a modified Wick theorem still holds for Fermi superoperators. It is given by Eq. (74) with the following changes. (i) We must use L,R rather than $+,-$ variables for ν. (ii) Each term needs to be multiplied by $(-1)^P$, where P is the number of permutations of elementary operators required to bring them to the specified order. Since left and right superoperators commute, we count only the number of permutations among left and among right operators. (Permuting a right and left operator does not count in P.)

The expectation of the T product of any number of (boson or fermion) superoperators may thus be expressed as the sum of all possible products of expectations of T products of the separated pairs of operators for the reference many-particle density matrix ρ_0 corresponding to H_0.

VII. DISCUSSION

Hilbert space and Liouville space offer a very different language for the description of nonlinear response. The density matrix provides a fully time-ordered description, since we only need to propagate it forward in time. In contrast, the wavefunction involves both forward and backward propagations. The choice is between following the ket only, moving forward and backward, or following the joint dynamics of the ket and the bra and moving only forward. Artificial time variables (Keldysh loops) commonly used in many-body theory [20,21,46] are connected with the wave function picture. The density matrix uses the real laboratory time scale throughout the calculation.

In Liouville space all observables are time ordered, leading naturally to a semiclassical approximations [28] and Feynman path integral diagrammatic techniques [1–7]. Maintaining time ordering allows us to recast $S^{(n)}$ using nonlinear response functions which decouple the field and the material parts. The nonlinear response function is calculated as a path integral in Liouville space by summing over the various possible pathways in Liouville space that contribute to the polarization. Path integrals have been extensively used as a useful tool for numerical computations of mixed quantum-classical calculations [65–67]. The density matrix formulation provides a similar development for phase space based numerical procedures. Graphical visualization of these paths is provided by double-sided Feynman diagrams [23].

The density matrix Liouville space picture offers many attractive features. The physical observables are directly and linearly related to the density matrix. Consequently, every step and intermediate quantity appearing in the description has a simple physical meaning and a clear classical analog. This should be contrasted with wave function based calculations of the transition amplitude, which by itself is not an observable, since signals are related to sums of products of such amplitudes.

The density matrix provides a practical way of performing ensemble averagings and developing reduced descriptions where bath degrees of freedom are traced out from the outset. Since it represents the state of the system by a matrix rather than a vector, an N-point grid for $\mathbf{p}$ and $\mathbf{q}$ in a semiclassical picture will require N^2 points for the wave function and N^4 for the density matrix. The ability to perform ensemble averagings and obtain reduced descriptions more than compensates for this price for complex systems. Many-body theory of superoperators further naturally allows for the treatment of dephasing and decoherence effects. Diagonal and off-diagonal elements of the density matrix are known as *populations* and *coherences*, respectively. When an off-diagonal element evolves in time for a system coupled to a bath, it acquires a phase, since its evolution from the left (ket) and the right (bra) is governed by different bath Hamiltonians. This phase depends on the state of the bath. When we perform an ensemble average of these elements over the distribution of the bath degrees of freedom, this variable phase results in a damping of these elements. The damping of off-diagonal elements of the density matrix resulting from phase (as opposed to amplitude) fluctuations is called *pure dephasing* or phase relaxation (also known as *decoherence*). Dephasing processes can be visualized in Liouville space only by following simultaneously the evolution of the bra and of the ket and maintaining the bookkeeping of their joint state. Dephasing processes directly affect all spectroscopic observables since they control the coherence, which is the window through which the system is observed. Different pathways representing distinct sequences of populations and coherences are naturally separated in Liouville space.

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APPENDIX: SOME USEFUL RELATIONS FOR SUPEROPERATOR ALGEBRA IN LIOUVILLE SPACE

A Liouville space operator A_α is labeled by a Greek subscript where $\alpha = L, R, +, -$. It is defined by its action on X, an ordinary (Hilbert space) operator. We write a general matrix element

$$(A_\alpha X)_{ij} \equiv \sum_{\kappa\ell} (A_\alpha)_{ij,\kappa\ell} X_{\kappa\ell}. \tag{A1}$$

A_α is thus a *tetradic* operator with four indices. Since $A_L X \equiv AX$ and $A_R X \equiv XA$, we obtain using Eq. (A1)

$$(A_L)_{ij,\kappa\ell} = A_{i\kappa}\delta_{j\ell}, \tag{A2}$$

$$(A_R)_{ij,\kappa\ell} = A_{\ell j}\delta_{i\kappa}. \tag{A3}$$

Note that the order of the $j\ell$ indices in Eq. (A3) has been reversed.

Since $A_+ \equiv \frac{1}{2}(A_L + A_R)$ and $A_- \equiv A_L - A_R$, we have $(A_-)_{ij,\kappa\ell} = A_{i\kappa}\delta_{j\ell} - A_{\ell j}\delta_{i\kappa}$ and $(A_+)_{ij,\kappa\ell} = \frac{1}{2}[A_{i\kappa}\delta_{j\ell} + A_{\ell j}\delta_{i\kappa}]$. It then follows that $[A_L, B_R] = 0$. This commutativity of left and right operators is possible thanks to the large size of the Liouville space and simplifies algebraic manipulations, resulting in many useful relations:

$$\begin{gathered}
2[A_+, B_-] = [A_L, B_L] - [A_R, B_R] = (AB)_- - (BA)_-, \\
\exp(A_L) = \exp(A_+)\exp\left(\frac{1}{2}A_-\right), \\
\exp(A_+) = \exp\left(\frac{1}{2}A_L\right)\exp\left(\frac{1}{2}A_R\right), \\
\exp(A_-) = \exp(A_L)\exp(-A_R), \\
(\exp A)_+ = 2\exp(A_+)\cosh\left(\frac{1}{2}A_-\right), \\
(\exp A)_- = 2\exp(A_+)\sinh\left(\frac{1}{2}A_-\right).
\end{gathered} \tag{A4}$$

In the following a is a complex number:

$$\begin{gathered}
\delta(\omega - A_-) = \int da\, \delta(a - A_L)\,\delta(\omega - a + A_R), \\
\delta(\omega - A_+) = \int da\, \delta(a - A_L)\,\delta(\omega - a - A_R), \\
\delta(a - A_L)\,\delta(a - A_R) = \delta(A_+ - a)\,\delta(A_-).
\end{gathered} \tag{A5}$$

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