

Quantum vs classical calculation of nonlinear spectra-reduced dynamics and intramolecular entropy

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A non-Markovian reduced equation of motion (REM) is derived for a generating function $P(a, t; a')$ which allows the calculation of two-time correlation functions in nonlinear systems. The form of the REM is identical for classical and quantum systems and it depends on an entropy function $\ln g(a)$, a velocity kernel $W(a, a')$, and a non-Markovian kernel $K(a, a', t)$, a being the expectation value of the dynamical variable under consideration. We give exact formal expressions for these quantities for the quantum and the classical case. In the linear (harmonic) limit the REM reduces rigorously to a non-Markovian Fokker-Planck equation. The present approach may allow a convenient and a systematic way for the calculation and the comparison of classical and quantum nonlinear spectra.

I. INTRODUCTION

The problem of nonlinear dynamics of intermediate size microscopic systems with two or more degrees of freedom has triggered an extensive theoretical effort in recent years. In classical mechanics this is an old problem connected all the way back to stellar dynamics.¹⁻³ It is well established that some of the classical trajectories in nonlinear systems are quasiperiodic whereas others are stochastic or chaotic. Studies of model systems show that the fraction of the phase space filled by the stochastic trajectories increases with the available energy. A convenient method to display this behavior is provided by the Poincaré surfaces of section. The quantum mechanical implications of these types of behavior are not at all clear. Many attempts have been made to define quantum stochasticity and this issue is currently the subject of a lively debate.⁴⁻⁹

In the field of molecular spectroscopy and dynamics we are interested in understanding the mechanisms, time scales and pathways for the flow of internal excitation in highly vibrationally activated polyatomic molecules. A basic problem in molecular spectroscopy is the development of efficient and accurate methods for the calculation of infrared (vibrational) and optical (electronic) spectra of molecules whose potential surfaces are not harmonic and whose intramolecular dynamics is therefore nonlinear. Such methods are crucial for relating the observable spectra to the intramolecular dynamics. It would be extremely useful if classical or semiclassical concepts could be implemented towards that goal and indeed much progress has been made in recent years in developing classical methods for the calculation of spectra. A major advantage of such methods is that they save the tedious calculation of the molecular eigenstates and allow the direct calculation of the spectra from the potentials of interaction.^{4,10,11} It should be noted, however, that the most detailed and highly resolved polyatomic molecular spectra are obtained from the excitation of ultracold molecules in supersonic beams, with initial vibrational temperatures of ~ 1 K.¹² This technique eliminates various sources of

inhomogeneous broadening which usually dominate these spectra and reveals valuable information on intramolecular dynamics. In this limit of ultracooled molecules, quantum effects are very significant and the usage of semiclassical methods must be made with extreme caution. The exact relevance of the semiclassical calculations to quantum molecular systems is therefore not at all clear. The Wigner distribution provides in principle a key to the connection between classical and quantum observables.¹³⁻¹⁶ However, it is a function of the entire phase space and as such contains too much information and it is quite difficult to calculate it properly for realistic systems.

In this paper we develop a *reduced description*, i. e., a non-Markovian reduced equation of motion (REM) which enables us to calculate quantum and classical correlation functions (and spectra) in a very similar way, thus allowing for a simple comparison. The present approach is based on a time convolutionless formalism which was proven recently to be very useful and suitable for spectroscopic studies.¹⁷⁻¹⁹ The solution to our REM results in a generating function $P(a, t; a')$ from which we can calculate the correlation functions of interest. The REM depends on three quantities which contain the microscopic dynamics: An entropy function $\ln g(a)$, a velocity kernel $W(a, a')$, and a non-Markovian kernel $K(a, a', t)$. The form of the REM is identical for the quantum and the classical cases and the difference is reflected in these three quantities. The plan of this paper is as follows: In Sec. II we introduce the basic notation and define the generating function. In Sec. III we derive the non-Markovian REM for the generating function and in Sec. IV we show that for a harmonic system the REM reduces simply to a Fokker-Planck equation. Finally, Sec. V contains a discussion and some concluding remarks.

II. CORRELATION FUNCTIONS AND LIOUVILLE SPACE DYNAMICS

We consider a system of N coupled nonlinear oscillators whose Hamiltonian is

$$H = \sum_{\nu=1}^N \frac{1}{2m_{\nu}} P_{\nu}^2 + V(Q_1, \dots, Q_N). \quad (1)$$

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Here m_ν , P_ν and Q_ν are the mass, the momentum and the coordinate of the ν 'th oscillator. V is the potential of interaction.

We shall be interested in calculating two time correlation functions of dynamical variables associated with this Hamiltonian. These are defined as follows: Given two operators A and B , their quantum mechanical correlation function is defined as

$$\langle A(\tau)B(0) \rangle_Q \equiv \text{Tr} [A^\dagger(\tau)B(0)\rho_Q]. \quad (2)$$

Here ρ_Q is the quantum mechanical canonical density matrix

$$\rho_Q \equiv \exp(-H/kT) / \text{Tr} \exp(-H/kT), \quad (3)$$

and $A(\tau)$ satisfies the Heisenberg equation of motion:

$$\dot{A} = i[H, A], \quad (4)$$

whose solution is

$$A(\tau) = \exp(iH\tau) A \exp(-iH\tau). \quad (5)$$

Upon introducing a complete basis set α, β, \dots , of eigenstates of H with energies E_α, E_β we may rewrite Eq. (2) in the form

$$\langle A(\tau)B(0) \rangle_Q = \sum_{\alpha, \beta} P(\alpha) A_{\alpha\beta}^\dagger B_{\beta\alpha} \exp(i\omega_{\alpha\beta}\tau), \quad (2a)$$

where $P(\alpha) \equiv \langle \alpha | \rho_Q | \alpha \rangle$, and $\omega_{\alpha\beta} \equiv E_\alpha - E_\beta$. In classical mechanics the dynamical variables A and B are functions in the phase space (\mathbf{P}, \mathbf{Q}) of the system. Their correlation function is defined as

$$\begin{aligned} \langle A(\tau)B(0) \rangle_c &\equiv \int d\mathbf{P}_0 d\mathbf{Q}_0 A(\tau | \mathbf{P}_0, \mathbf{Q}_0) \\ &\times B(\mathbf{P}_0, \mathbf{Q}_0) \rho_c(\mathbf{P}_0, \mathbf{Q}_0), \end{aligned} \quad (6)$$

where

$$\rho_c = \exp(-H/kT) / \int d\mathbf{P} d\mathbf{Q} \exp(-H/kT), \quad (7)$$

is the classical density matrix. $A(\tau | \mathbf{P}_0, \mathbf{Q}_0)$ satisfies the classical Liouville equation,

$$\dot{A} = -i\{H, A\}, \quad (8)$$

with the initial condition $A(0 | \mathbf{P}_0, \mathbf{Q}_0) \equiv A(\mathbf{P}_0, \mathbf{Q}_0)$. Here $\{, \}$ is the Poisson brackets:

$$\{H, A\} \equiv \sum_\nu \left[\frac{\partial H}{\partial Q_\nu} \frac{\partial A}{\partial P_\nu} - \frac{\partial H}{\partial P_\nu} \frac{\partial A}{\partial Q_\nu} \right]. \quad (9)$$

In the frequency domain we define

$$\begin{aligned} I(\omega) &\equiv -i \int_0^\infty d\tau \exp(i\omega\tau) \langle A(\tau)B(0) \rangle \\ &\equiv I'(\omega) - iI''(\omega), \end{aligned} \quad (10)$$

where I' and I'' stand for the real and imaginary parts, respectively. When A and B are taken to be the dipole operator for the radiation-matter interaction then $I''(\omega)$ is the absorption spectrum.

For the subsequent manipulations it will be useful to work in Liouville space and to adopt a common notation for classical and quantum systems.²⁰⁻²² In Liouville space we treat ordinary dynamical variables as vectors. We define a ket $|A\rangle$ corresponding to an ordinary

operator A and a bra $\langle\langle A|$ corresponding to A^\dagger . We further define a scalar product in Liouville space as follows:

$$\langle\langle A|B\rangle\rangle \equiv \int d\Gamma A^\dagger B \rho \equiv \begin{cases} \text{Tr} A^\dagger B \rho_Q & \text{quantum mechanics,} \\ \iint d\mathbf{P} d\mathbf{Q} A^\dagger B \rho_c & \text{classical mechanics.} \end{cases} \quad (11)$$

$\int d\Gamma$ thus stands for a trace in quantum mechanics and for an integration over phase space in classical mechanics.

We further write both Eqs. (4) and (8) in the form:

$$\frac{dA}{dt} = iLA, \quad (12)$$

where L is the Liouville operator:

$$LA \equiv \begin{cases} [H, A] & \text{quantum mechanics,} \\ i\{H, A\} & \text{classical mechanics.} \end{cases} \quad (12a)$$

In Liouville space L is a superoperator with "matrix elements"

$$\langle\langle A|L|B\rangle\rangle \equiv \int d\Gamma A^\dagger L B \rho. \quad (13)$$

Using these definitions we can write both the classical and the quantum mechanical correlation functions in the form:

$$\langle A(\tau)B(0) \rangle \equiv \langle\langle A(\tau)|B\rangle\rangle = \langle\langle A|\exp(-iL\tau)|B\rangle\rangle, \quad (14)$$

where

$$\begin{aligned} |A(\tau)\rangle &= \exp(iL\tau) |A\rangle, \\ \langle\langle A(\tau)| &= \langle\langle A|\exp(-iL\tau). \end{aligned} \quad (14a)$$

In the forthcoming manipulations we shall extensively use operators of the form $\delta(a-A)$, where δ is the Dirac δ function. $\delta(a-A)$ is a function of the operator A that depends on the parameter a . We shall therefore review now some of the properties of $\delta(a-A)$.²³

(1) $\delta(a-A)$ can be used to generate any function of the operator A via the relation:

$$\int \delta(a-A) f(a) da = f(A). \quad (15)$$

(2) Normalization:

$$\int \delta(a-A) da = 1. \quad (16)$$

(3)

$$\langle\langle \delta(a-A) \rangle\rangle \equiv \int d\Gamma \delta(a-A) \rho \equiv g(a), \quad (17)$$

$g(a)$ is a measure of the volume in phase space compatible with the constraint that the operator A has the value a . Consequently $\ln g(a)$ is related to the entropy associated with the operator A [see Eqs. (46)] and will play a significant role in our reduced description of the system. Equations (16) and (17) imply that

$$\int g(a) da = 1. \quad (18)$$

(4) Let us consider a complete set of functions of one variable $\{\phi_n\}$ which satisfy the following orthonormality conditions:

$$\langle \phi_n | \phi_m \rangle \equiv \int da g(a) \phi_n^*(a) \phi_m(a) = \delta_{n,m}. \quad (19)$$

Using Eq. (19), then the scalar product $\langle \langle \phi_n(A) | \phi_m(A) \rangle \rangle$ is given by

$$\begin{aligned} \langle \langle \phi_n(A) | \phi_m(A) \rangle \rangle &\equiv \int d\Gamma \phi_n^*(A) \phi_m(A) \rho \\ &= \int d\Gamma \phi_n^*(A) \phi_m(A) \rho \int da \delta(a-A) \\ &= \int da \phi_n^*(a) \phi_m(a) g(a) = \delta_{n,m}. \end{aligned} \quad (20)$$

We can therefore define the following projection operator in Liouville space:

$$\hat{P} = \sum_n |\phi_n(A)\rangle \langle \langle \phi_n(A) | \rangle. \quad (21)$$

Equation (20) guarantees that \hat{P} is indeed a projection operator, i. e., $\hat{P}^2 = \hat{P}$. When \hat{P} acts on an arbitrary dynamical variable it expands it in a power series of A . Since, in general, A, A^2, \dots are not a complete set of operators then \hat{P} is a projection (otherwise \hat{P} would have been simply the unit operator). However, when \hat{P} acts on an operator which depends only on A then it is equivalent to the unit operator! We therefore have

$$\begin{aligned} |\delta(a-A)\rangle &= \hat{P} |\delta(a-A)\rangle \\ &= \sum_n |\phi_n(A)\rangle \langle \langle \phi_n(A) | \delta(a-A) \rangle \rangle \\ &= \sum_n |\phi_n(A)\rangle g(a) \phi_n(a), \end{aligned} \quad (22)$$

i. e., if we drop the bra, ket notation:

$$\delta(a-A) = g(a) \sum_n \phi_n^*(A) \phi_n(a). \quad (23)$$

Equation (23) is very useful since it allows us to expand $\delta(a-A)$ in a basis set of functions which satisfy the orthonormality condition [Eq. (19)]. Note that if $g(a)$ is Gaussian then ϕ_n are the Hermite polynomials.

$$(5) \langle \langle \delta(a-A) | \delta(a'-A) \rangle \rangle = g(a) \delta(a-a'). \quad (24)$$

The functions $\delta(a-A)/\sqrt{g(a)}$ therefore form a continuous set of orthonormal functions of A and they can be used in the projection operator \hat{P} [Eq. (21)] as well, resulting in

$$\hat{P} = \int da g(a)^{-1} |\delta(a-A)\rangle \langle \langle \delta(a-A) | \rangle. \quad (25)$$

This projection operator [Eq. (21) or (25)] performs coarse graining of the phase space according to the expectation value of A . In the next section, we shall make use of properties (1)–(5) to derive our non-Markovian REM which will be used to calculate the correlation functions of A .

III. THE GENERATING FUNCTION FOR TWO TIME CORRELATION FUNCTIONS

We shall consider a single dynamical variable A and we wish to evaluate a correlation function of some func-

tions of A , i. e.,

$$\begin{aligned} \langle \langle f(A(\tau)) f'(A) \rangle \rangle &\equiv \langle \langle f(A) | \exp(-iL\tau) | f'(A) \rangle \rangle \\ &= \int d\Gamma f^*(A(\tau)) f'(A) \rho(\Gamma), \end{aligned} \quad (26)$$

f and f' being two arbitrary functions. To that end, we shall define the following quantity:

$$\begin{aligned} P(a, t; a') &\equiv \langle \langle \delta(a-A) | \exp(-iLt) | \delta(a'-A) \rangle \rangle \\ &= \langle \langle \delta(a-A(t)) | \delta(a'-A) \rangle \rangle. \end{aligned} \quad (27)$$

Making use of Eq. (15) we immediately have

$$\langle \langle f(A(\tau)) f'(A) \rangle \rangle = \iint f^*(a) f'(a') P(a, \tau; a') da da'. \quad (28)$$

$P(a, \tau; a')$ is therefore a *generating function* which allows us to calculate any correlation function of the form [Eq. (26)]. From the definition, Eqs. (27) and (16), it immediately follows that P satisfies the following normalization conditions:

$$\int P(a, \tau; a') da' = g(a), \quad (29a)$$

$$\int P(a, \tau; a') da = g(a'), \quad (29b)$$

and

$$P(a, 0; a') = g(a') \delta(a-a'). \quad (29c)$$

We are using here the common notation from the theory of stochastic processes²⁴ where $P(a, \tau; a')$ denotes the joint probability for the variable A to assume the value a' at time 0 and the value a at time τ . In classical mechanics $P(a, \tau; a')$ is indeed a joint probability. It is real, positive and normalized [Eqs. (29)]. In quantum mechanics however P will be in general complex so that strictly speaking it is not a probability. It should be noted that by adopting a different definition of the scalar product [Eq. (11)] it is possible to make P real also in the quantum case [see Eqs. (66) and (67) in the Discussion]. The important property of P is Eq. (28) which holds equally well for quantum and classical systems. Our goal will now be to derive an equation of motion for P . This is done in the Appendix using a time convolutionless projection operator formalism which was proven to be extremely effective for a variety of nonequilibrium problems.¹⁷ We finally get the following *exact* equation which holds for quantum as well as classical systems:

$$\begin{aligned} \frac{dP(a, t; a')}{dt} &= -\frac{\partial}{\partial a} \int da'' W(a, a'') P(a'', t; a') / g(a'') \\ &+ \int_0^t d\tau \int da'' \frac{\partial}{\partial a} \sqrt{g(a)} K(a, a'', \tau) \sqrt{g(a')} \frac{\partial}{\partial a'}, \\ &\times \frac{P(a'', t; a')}{g(a'')}. \end{aligned} \quad (30)$$

With the initial conditions:

$$P(a, 0; a') = g(a') \delta(a-a'). \quad (31)$$

Here

$$-\frac{\partial}{\partial a} W(a, a'') \equiv \dot{\chi}(a, a'', 0) \quad (32)$$

and

$$\frac{\partial}{\partial a} \sqrt{g(a)} K(a, a', \tau) \sqrt{g(a'')} \frac{\partial}{\partial a'} \\ = \sqrt{\frac{g(a'')}{g(a)}} [\ddot{\chi}(\tau) - \dot{\chi}(\tau)\chi^{-1}(\tau)\dot{\chi}(\tau)] \\ \times \left[1 + \frac{1}{g} \int_0^\tau d\tau_1 \dot{\chi}(\tau_1) \right]^{-1}. \quad (33)$$

The operator χ is defined as follows:

$$\chi(a, a', t) \equiv \langle\langle \delta(a-A) | \exp(-iLt) | \delta(a''-A) \rangle\rangle \\ = g(a) \delta(a-a'') + \int_0^t d\tau \dot{\chi}(a, a', \tau), \quad (34a)$$

$$\dot{\chi}(a, a', t) \equiv -i \langle\langle \delta(a-A) | L \exp(-iLt) | \delta(a''-A) \rangle\rangle \\ = \langle \delta(a-A) \exp(-iL\tau) \dot{A} \delta(a''-A) \rangle \frac{\partial}{\partial a''} \\ = -\frac{\partial}{\partial a} \langle \delta(a-A) \dot{A} \exp(-iL\tau) \delta(a''-A) \rangle \quad (34b)$$

and

$$\ddot{\chi}(a, a', t) \equiv (-i)^2 \langle\langle \delta(a-A) | L \exp(-iLt) L | \delta(a''-A) \rangle\rangle \\ = \frac{\partial}{\partial a} \langle \delta(a-A) \dot{A} \exp(-iL\tau) \dot{A} \delta(a''-A) \rangle \frac{\partial}{\partial a''}. \quad (34c)$$

The $\delta(a-A)$ in Eqs. (34) may be represented via the expansion (23) and the operation is a symmetrization, i. e.,

$$\underline{A\dot{A}} \equiv \frac{1}{2} [A\dot{A} + \dot{A}A], \quad (35a)$$

$$\underline{A^2\dot{A}} \equiv \frac{1}{3} [A^2\dot{A} + A\dot{A}A + \dot{A}A^2], \quad (35b)$$

etc. It should be noted that since $\chi(a, a', t) \equiv P(a, t; a')$, Eq. (30) may seem at first glance to be of very little use since in order to derive the equation we apparently need to know its solution in advance. Therefore, the equation seems to give us back what we already knew! This is however a false impression. In order to use this equation in a constructive way we should develop approximation schemes towards the calculation of $g(a)$, $W(a, a')$, and $K(a, a', t)$. It is true that the exact knowledge of these quantities is equivalent to the knowledge of $P(a, t; a')$. However, when we use some low order approximations for g , W , and K , Eq. (30) results in an infinite order approximation for P . In other words, Eq. (30) is a convenient means to generate *partial resummation* of diagrammatic expansions for P . Some problems where such expansions were made within the time convolutionless approach are collisional broadening of spectral lines and energy transfer in disordered systems. The types of expansions made there are perturbation theory, a density expansion and a long wavelength (hydrodynamic) expansion.¹⁷ Making use of the Kramers-Moyal expansion²⁵ we can alternatively represent the operators $\dot{\chi}$ and $\ddot{\chi}$ in a local representation, i. e.,

$$\dot{\chi} = \sum_{n=0}^{\infty} \frac{1}{n!} \langle \delta(a-A) \exp(-iLt) \underline{A}(a-A)^n \rangle \frac{\partial^{n+1}}{\partial a^{n+1}}, \quad (36a)$$

$$\ddot{\chi} = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{\partial}{\partial a} \langle \delta(a-A) \underline{A} \exp(-iLt) \underline{A}(a-A)^n \rangle \frac{\partial^{n+1}}{\partial a^{n+1}}. \quad (36b)$$

Equation (30) is the main result of the present paper. It enables us to calculate classical and quantum correlation functions in a very similar fashion. The microscopic dynamics in this equation is contained in the following quantities:

(1) $g(a)$ which is a measure of the volume in phase space compatible with the constraint $A = a$.

(2) $W(a, a')$ which is a time independent velocity kernel. Note that the W term in the right-hand side of Eq. (30) gives the time derivative of P at $t = 0$. In the classical case W may be further simplified and assumes a local form:

$$W(a, a')/g(a'') = \langle\langle \delta(a-A) \dot{A} | \delta(a''-A) \rangle\rangle/g(a'') \\ = V(a) \delta(a-a'), \quad (37)$$

where

$$V(a) \equiv \langle \dot{A} \delta(a-A) \rangle/g(a) \quad (37a)$$

is the mean "velocity" (\dot{A}) on the "microcanonical" surface $\delta(a-A)$. The first term in the right-hand side of Eq. (30) then assumes the familiar form²⁶:

$$\int da' W(a, a') P(a', t; a')/g(a') \\ - - \frac{\partial}{\partial a} [V(a) P(a, t; a')]. \quad (38)$$

In the quantum case, however, we should retain the nonlocal form of W .

(3) The time dependent kernel $K(a, a', t)$. Note that the $\sqrt{[g(a'')/g(a)]}$ factor in the definition of K [Eq. (33)] makes it symmetric, i. e., $K(a, a', t) = K(a'', a, t)$.

$\ln g(a)$ is particularly interesting since it represents a generalized *intramolecular entropy*. To see that, we first note that $g(a)$ is a real and a nonnegative quantity. This may be seen by expanding Eq. (17) in a basis set of eigenfunctions of the operator $A, \{|\phi_\gamma\rangle\}$ with eigenvalues γ . We then have

$$g(a) = \sum_\gamma \langle \phi_\gamma | \rho_0 | \phi_\gamma \rangle \delta(a-\gamma), \quad (39)$$

where the summation should be replaced by an integration should the spectrum of A be continuous. Since the diagonal elements of the density matrix are nonnegative, this makes $g(a)$ to be nonnegative too.

The partition function of the system is given by

$$Z_0(T) \equiv \int d\Gamma \exp(-H/kT). \quad (40)$$

Similarly, we can define a generalized partition function $Z(a, T)$ and a mean energy $\bar{E}(a, T)$ subject to the constraint that the variable A assumes the value a , i. e.:

$$Z(a, T) \equiv \int d\Gamma \exp(-H/kT) \delta(a-A), \quad (41)$$

$$\bar{E}(a, T) \equiv \frac{1}{Z(a, T)} \int d\Gamma H \exp(-H/kT) \delta(a-A). \quad (42)$$

We can now introduce a free energy $G(a, T)$ and an entropy function $S(a, T)$ associated with the variable A ,

via the identities:

$$Z(a, T) = \exp[-G(a, T)/kT] \quad (43)$$

and

$$G(a, T) \equiv \bar{E}(a, T) - TS(a, T). \quad (44)$$

Using Eqs. (17), (40), and (41) we have

$$Z(a, T) = Z_0(T) g(a, T), \quad (45)$$

where for the sake of clarity we have written explicitly the dependence of g on T , $g(a, T) \equiv g(a)$. Using Eqs. (43)–(45), we finally get

$$G(a, T) = -kT \ln Z_0(T) - kT \ln g(a, T) \quad (46a)$$

and

$$S(a, T) = \bar{E}(a, T)/T + k \ln Z_0(T) + k \ln g(a, T). \quad (46b)$$

We thus see that $\ln g(a)$ is a measure of the free energy or entropy associated with the variable A . Let us consider now a simple but useful limit. Assuming that

$$\int_0^t d\tau K(a, a', \tau) = \delta(a - a') \phi_1(t), \quad (47a)$$

and

$$W(a, a'') = \phi_2 g(a'') \frac{\partial}{\partial a''} \delta(a - a''), \quad (47b)$$

where $\phi_1(t)$ is some function of time, and ϕ_2 is a constant, Eq. (30) reduces the non-Markovian Fokker-Planck equation:

$$\frac{\partial P}{\partial t} = \phi(t) \frac{\partial}{\partial a} \left[g(a) \frac{\partial}{\partial a} \left(\frac{P}{g(a)} \right) \right], \quad (48)$$

where

$$\phi(t) \equiv \phi_1(t) + \phi_2. \quad (48a)$$

Equation (48) may be rearranged in the form:

$$\frac{dP}{dt} = \phi(t) \left[\frac{\partial^2 P}{\partial a^2} - \frac{\partial}{\partial a} \left(\frac{\partial \ln g}{\partial a} P \right) \right], \quad (48b)$$

where $P \equiv P(a, t; a')$ and the initial condition is as before [Eq. (31)]. We shall see in the next section that Eq. (48b) is *exact* for a harmonic system.

IV. THE GENERATING FUNCTION FOR A HARMONIC SYSTEM

Consider a system of harmonic oscillators (quantum or classical) described by the Hamiltonian:

$$H = \sum_{\nu} \left[\frac{1}{2m_{\nu}} P_{\nu}^2 + \frac{1}{2} m_{\nu} \omega_{\nu}^2 Q_{\nu}^2 \right]. \quad (49)$$

Here m_{ν} and ω_{ν} are the mass and the frequency of the ν th oscillator. Let us consider the following dynamical variable A :

$$A \equiv \sum_{\nu} c_{\nu} Q_{\nu}. \quad (50)$$

This operator may represent, e.g., the dipole operator for a harmonic molecule where c_{ν} is the transition dipole of the ν th normal mode. We shall be interested in evaluating

$$P(a, t; a') \equiv \langle \delta(A(t) - a) \delta(A - a') \rangle, \quad (51)$$

where A is given by Eq. (50) and the time evolution is governed by the Hamiltonian Eq. (49). This may be evaluated by standard methods. Performing a Fourier transformation, we get

$$P(a, t; a') = \frac{1}{4\pi^2} \int dk \int dk' \exp[i(ka - k'a')] \times \langle \exp[-ikA(t)] \exp(ik'A) \rangle. \quad (52)$$

Making use of the cumulant expansion,²⁷ we have

$$\langle \exp(-ikA(t)) \exp(ik'A) \rangle = \exp \left[\frac{-\Delta^2}{2} (k^2 + k'^2 - 2kk'\rho) \right], \quad (53)$$

where

$$\Delta^2 \equiv \langle A^2 \rangle = \sum_{\nu} c_{\nu}^2 \langle Q_{\nu}^2 \rangle, \quad (54a)$$

$$\rho(t) \equiv \langle A(t)A \rangle / \langle A^2 \rangle = \sum_{\nu} c_{\nu}^2 \langle Q_{\nu}(t)Q_{\nu} \rangle / \Delta^2. \quad (54b)$$

Upon substitution Eq. (53) in Eq. (52) and performing the Fourier transformations, we finally get:

$$P(at; a') = \frac{1}{\sqrt{2\pi\Delta}\sqrt{1-\rho^2}} \times \exp \left[-\frac{(a-a'\rho)^2}{2\Delta^2(1-\rho^2)} \right] \cdot g(a'), \quad (55)$$

where

$$g(a') = \frac{1}{\sqrt{2\pi\Delta}} \exp \left(-\frac{a'^2}{2\Delta^2} \right). \quad (56)$$

Note that Eq. (55) holds equally well for quantum and classical oscillators, the only difference is in the quantities Δ and $\rho(t)$. For a quantum mechanical system we have

$$\Delta^2 = \sum_{\nu} \frac{\hbar^2 c_{\nu}^2}{2m_{\nu} \omega_{\nu}} (2\bar{n}_{\nu} + 1), \quad (57a)$$

and

$$\rho(t) = \sum_{\nu} \frac{\hbar^2 c_{\nu}^2}{2m_{\nu} \omega_{\nu}} [(\bar{n}_{\nu} + 1) \exp(-i\omega_{\nu}t) + \bar{n}_{\nu} \exp(i\omega_{\nu}t)] / \Delta^2, \quad (57b)$$

where

$$\bar{n}_{\nu} = [\exp(\hbar\omega_{\nu}/kT) - 1]^{-1}. \quad (57c)$$

For classical oscillators we have

$$\Delta^2 = \sum_{\nu} \frac{kT}{m_{\nu} \omega_{\nu}^2} c_{\nu}^2, \quad (58a)$$

and

$$\rho(t) = \sum_{\nu} \frac{kT c_{\nu}^2}{m_{\nu} \omega_{\nu}^2 \Delta^2} \cos \omega_{\nu}t. \quad (58b)$$

By simple inspection we note that P as given by Eq. (55) satisfies the following equation:

$$\frac{\partial P}{\partial t} = -\frac{\dot{\rho}(t)}{\rho(t)} \left[\frac{\partial}{\partial a} (aP) + \Delta^2 \frac{\partial^2 P}{\partial a^2} \right] \quad (59)$$

with the initial condition:

$$P(a, t; a') = g(a) \delta(a - a'). \quad (59a)$$

Clearly this equation is a special case of Eq. (30) [and Eq. (48b)] and it may be obtained from Eq. (30) by substituting

$$g(a) = \frac{1}{\sqrt{2\pi}\Delta} \exp(-a^2/2\Delta^2), \quad (60a)$$

$$W(a, a'') = \Delta^2 \dot{\rho}(0) g(a'') \frac{\partial}{\partial a''} \delta(a - a''), \quad (60b)$$

$$\int_0^t d\tau K(a, a'', \tau) = - \left[\frac{\dot{\rho}(t)}{\rho(t)} - \dot{\rho}(0) \right] \Delta^2 \delta(a - a''). \quad (60c)$$

Equation (55) may be used to evaluate any correlation function of A . As an example, let us evaluate:

$$I''(\omega) \equiv \frac{1}{2} \int_{-\infty}^{\infty} d\tau \exp(i\omega\tau) \langle A(\tau)A(0) \rangle, \quad (61a)$$

where

$$\langle A(\tau)A(0) \rangle = \int da \int da' a a' p(a, t; a'). \quad (61b)$$

Upon substituting Eq. (55) into Eq. (61b) we finally get classically:

$$I''_c(\omega) = \pi \sum_{\nu} c_{\nu}^2 \frac{kT}{2m_{\nu}\omega_{\nu}^2} [\delta(\omega - \omega_{\nu}) + \delta(\omega + \omega_{\nu})], \quad (62a)$$

and quantum mechanically:

$$I''_Q(\omega) = \pi \sum_{\nu} \frac{\hbar c_{\nu}^2}{2m_{\nu}\omega_{\nu}} [(\bar{n}_{\nu} + 1)\delta(\omega - \omega_{\nu}) + \bar{n}_{\nu}\delta(\omega + \omega_{\nu})]. \quad (62b)$$

Note that

$$I''_c(-\omega) = I''_c(\omega), \quad (63a)$$

whereas

$$I''_Q(-\omega) = \exp(-\hbar\omega/kT) I''_Q(\omega), \quad (63b)$$

which is a manifestation of the fluctuation dissipation theorem.²⁸

V. DISCUSSION

In this paper, we have developed a generalized non-Markovian reduced equation of motion [Eq. (30)] which has the same form for classical and quantum systems. The solution of this equation [$P(a, t; a')$] with the initial condition [Eq. (31)] is a generating function which allows us to calculate any two time correlation function associated with the dynamical variable A via Eq. (28). In the classical case $P(a, t; a')$ is the joint probability distribution of finding the variable A with the value a' at time 0 and the value a at time t . It is real and nonnegative. In the quantum case P is in general complex so that we cannot view it as a probability. The important point however is that in both cases Eq. (28) holds and P may be used to calculate the necessary correlation functions.

The microscopic information which enters this equation of motion is contained in the following quantities: Phase space volume (statistical weight) associated with A , $g(a)$, a velocity kernel [Eq. (32)] $W(a, a')$, and a symmetric, time dependent kernel $K(a, a'', t)$ [Eq. (33)]. The present REM [Eq. (30)] is very similar to the one commonly used in classical nonequilibrium statistical

mechanics.^{29,30} The main differences are the nonlocal first term $W(a, a')$ which in the classical limit reduces to the local form [Eq. (38)]. In addition our equation is local in time [the right-hand side of Eq. (30) depends only on $P(t)$] whereas the more conventional REM contains a convolution in time and the right-hand side will depend on $P(\tau)$ for $0 \leq \tau \leq t$. This time convolutionless formalism was developed recently and was shown to be particularly useful and efficient for Gaussian type processes.¹⁷⁻¹⁹ In the harmonic case, e.g., our kernel assumes a very simple form [Eq. (60c)] whereas the kernel corresponding to the other REM with the convolution will be very complicated, even in this simple case. Another advantage of the present derivation is that as noted by Nordholm and Zwanzig³⁰ it is basically the same for quantum and classical variables. The only difference is the \perp operation, which need not be made in the classical case.

In the case of a harmonic system we have shown that the generalized REM reduces to a non-Markovian Fokker-Planck equation [Eq. (59)], since in this case $W(a, a')$, $g(a)$, and $K(a, a'', t)$ assume the simple form [Eqs. (60)]. It is interesting to note the striking similarity between Eqs. (59) and (55) and the corresponding expressions for stochastic processes.²⁸ If a is a stationary Gaussian Markov Process then its probability distribution and equation of motion are given by Eqs. (55) and (59), respectively, but with

$$\rho(t) = \exp(-\gamma t), \quad (64a)$$

so that

$$\dot{\rho}/\rho = -\gamma. \quad (64b)$$

The variable A [Eq. (50)] for a harmonic system therefore behaves like a stationary Gaussian but non-Markov process. Physically what happens is that for a single oscillator $P(a, t; a')$ is a *periodic* function. At time $t = 0$ it is $\sim \delta(a - a')$. Then there is a *dephasing* process and it spreads into a Gaussian packet (due to the uncertainty in the initial momenta). At $\omega t = \pi/2$ there is a maximum dephasing and then a *rephasing* process occurs which brings P back to the $\sim \delta(a - a')$ form at $\omega t = \pi$, etc. This evolution goes on periodically. If the system consists of a few oscillators whose frequencies are *incommensurate* (their ratio is not rational) then the evolution is only *quasiperiodic* and the rephasing will not be perfect for any finite time. However, it is possible to come as closely as desired to a complete rephasing by going to longer and longer times. For a Markov process on the other hand, the dephasing is irreversible. The addition of anharmonicities to the Hamiltonian (49) will change the nature of the quasiperiodic time evolution [Eq. (57b)] and may turn it to be irreversible on the relevant time scales. It should be emphasized that we are *not* treating here a *Brownian oscillator* system (i.e., oscillators with an *external* random force), in spite the striking formal similarity between Eq. (55) and the joint probability for the later problem. The stochasticity comes here from the *reduction* (since we watch explicitly only the time evolution of A^n , $n = 1, 2, \dots$). The present formalism may provide a very convenient way for treating quantum and

classical correlation functions for nonlinear (anharmonic) systems, along the same footing. A nonlinear system is characterized by the Hamiltonian:

$$H = H_0 + V'(Q_1, \dots, Q_N), \quad (65)$$

where H_0 is given by Eq. (49). In that case we need to develop the perturbative expansions for $g(a)$, $W(a, a')$, and $K(a, a', t)$ as a function of V' and compare them for the quantum and the classical cases. Alternatively, we may develop a diagrammatic expansion directly for $P(a, t; a')$ using the methods developed by Kawasaki in the Mode coupling formalism.²³ It is clear that the present time convolutionless approach is far superior than the conventional formalism^{29,30} for that purpose since the relevant quantities g , W and K [Eqs. (60)] are extremely simple in the harmonic case and they form a convenient starting point for a diagrammatic expansion. The corresponding quantities for the conventional (convolution) formalism are much more complicated even for the harmonic case. For the sake of comparing quantum and classical spectra, it might be advantageous to adopt an alternative definition of the scalar product. Instead of Eq. (11) we define

$$\langle\langle A | B \rangle\rangle \equiv \frac{1}{2} \int d\Gamma [A^\dagger B \rho + B^\dagger A \rho] \quad (66)$$

so that

$$\langle\langle A(\tau) | B(0) \rangle\rangle \equiv \frac{1}{2} [\langle A(\tau) B(0) \rangle + \langle B(0) A(\tau) \rangle]. \quad (67)$$

It may be easily verified that this definition satisfies all the formal requirements of a scalar product (positive norm, etc.).³¹ Making use of the fluctuation dissipation theorem²⁸ we can later construct $\langle A(\tau) B(0) \rangle$ from $\langle\langle A(\tau) | B(0) \rangle\rangle$. This symmetrized scalar product makes $\langle\langle A | B \rangle\rangle$ real in the quantum and classical cases. In addition, we have $\langle\langle A | B \rangle\rangle = \langle\langle B | A \rangle\rangle$. The formalism developed in this paper will apply as it is for the new scalar product as well but $P(a, t; a')$ will now become real also quantum mechanically. Moreover, under certain general conditions such as when the operator A is invariant under time reversal, then $W(a, a'')$ will vanish identically provided we use the scalar product [Eq. (66)]. This will obviously simplify the analysis of the nonlinear case since only $K(a, a'', t)$ and $g(a)$ will have to be considered.

Finally, we note that the present formulation may be easily generalized to incorporate more general types of correlation functions containing several operators A_α $\alpha = 1, \dots, N$.^{23,30} In that case we define a multi-variable generating function:

$$P(\mathbf{a}, t; \mathbf{a}') \equiv \left\langle\left\langle \prod_{\alpha=1}^N \delta(a_\alpha - A_\alpha) \left| \exp(-iLt) \right| \prod_{\beta=1}^N \delta(a'_\beta - A'_\beta) \right\rangle\right\rangle, \quad (68)$$

where $\mathbf{a} \equiv (a_1, a_2, \dots, a_N)$ and the product of operators should be symmetrized in the quantum case.²³ Correspondingly we shall have $g(\mathbf{a})$, $W(\mathbf{a}, \mathbf{a}'')$, and $K(\mathbf{a}, \mathbf{a}'', t)$ as a direct generalization of Eqs. (31)–(33), and the derivative $\partial/\partial a$ in Eq. (30) will be replaced by $\sum_\alpha \partial/\partial a_\alpha$, i. e.,

$$\begin{aligned} \frac{\partial P(\mathbf{a}, t; \mathbf{a}')}{\partial t} = & - \sum_\alpha \frac{\partial}{\partial a_\alpha} \int d\mathbf{a}'' W(\mathbf{a}, \mathbf{a}'') P(\mathbf{a}'', t; \mathbf{a}') / g(\mathbf{a}'') \\ & + \sum_\alpha \sum_\beta \int_0^t d\tau \int d\mathbf{a}'' \frac{\partial}{\partial a_\alpha} \sqrt{g(\mathbf{a})} K(\mathbf{a}, \mathbf{a}'', \tau) \\ & \times \sqrt{g(\mathbf{a}'')} \frac{\partial}{\partial a'_\beta} \left(\frac{P(\mathbf{a}'', t; \mathbf{a}')}{g(\mathbf{a}'')} \right). \quad (69) \end{aligned}$$

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APPENDIX

In this appendix we shall derive the generalized master equation [Eq. (30)]. We first define the following operators:

$$\chi(a, a', t) \equiv \langle\langle \delta(a - A) | \exp(-iLt) | \delta(a' - A) \rangle\rangle \quad (A1)$$

and

$$\dot{\chi}(a, a', t) \equiv -i \langle\langle \delta(a - A) | L \exp(-iLt) | \delta(a' - A) \rangle\rangle. \quad (A2)$$

Of course $\chi(a, a', t) \equiv P(a, t; a')$. We can therefore write the trivial identity:

$$\dot{P} = [\dot{\chi}/\chi] P. \quad (A3)$$

Equation (A3) may be written more explicitly in the form:

$$\frac{dP(a, t; a')}{dt} = \int da'' g(a'') R(a, a'', t) P(a'', t; a'), \quad (A4)$$

where

$$R(t) \equiv \dot{\chi}(t)/\chi(t), \quad (A5)$$

i. e.,

$$\begin{aligned} R(a, a'', t) = & \int d\bar{a} g(\bar{a}) \dot{\chi}(a, \bar{a}, t) \\ & \times (\chi^{-1})(\bar{a}, a'', t). \quad (A6) \end{aligned}$$

Equation (A5) is a shorthand notation for Eq. (A6). To proceed further we again use a trivial identity:

$$R(t) = R(0) + \int_0^t d\tau \dot{R}(\tau) \quad (A7)$$

and get

$$R(0) = \dot{\chi}(0)/\chi(0), \quad (A8)$$

$$\dot{R}(\tau) = [\ddot{\chi}(\tau) - \dot{\chi}(\tau)\chi^{-1}(\tau)\dot{\chi}(\tau)]/\chi(\tau). \quad (A9)$$

Upon the substitution of Eqs. (A7)–(A9) in Eq. (A4) we get

$$\begin{aligned} \frac{dP(a, t; a')}{dt} = & \int da'' g(a'') R(a, a'', 0) P(a'', a'; t) \\ & + \int da'' g(a'') \int_0^t d\tau \dot{R}(a, a'', \tau) P(a'', t; a'). \quad (A10) \end{aligned}$$

In the classical case, using the definition of the Poisson brackets [Eq. (9)] we have

$$\begin{aligned} \frac{d}{dt} \delta(a-A) &= iL\delta(a-A) \\ &= \dot{A} \frac{\partial}{\partial a} \delta(a-A) = \frac{\partial}{\partial a} [\dot{A} \delta(a-A)] . \end{aligned} \quad (\text{A11})$$

This equation holds in the quantum case as well, provided we make the change:

$$iL \delta(a-A) = \frac{\partial}{\partial a} \dot{A} \delta(a-A) , \quad (\text{A12})$$

where \dot{A} means the following: We first expand $\delta(a-A)$ [Eq. (23)],

$$\delta(a-A) = g(a) \sum_n \phi_n(a) \phi_n(A) \quad (\text{A13})$$

and then we symmetrize all products of \dot{A} and A^n , i.e.:

$$\dot{A}A \equiv \frac{1}{2} [\dot{A}A + A\dot{A}] , \quad (\text{A14a})$$

$$\dot{A}A^2 \equiv \frac{1}{3} [\dot{A}A^2 + A\dot{A}A + A\dot{A}] , \quad (\text{A14b})$$

etc. of course in the classical case, we can ignore the \dot{A} sign since there is no problem of commutation.

Equation (A12) was used to get the right-hand side of Eqs. (34b) and (34c). Using this we may now evaluate $R(0)$,

$$\chi(a, a', 0) = \langle \delta(a-A) \delta(a'-A) \rangle = g(a) \delta(a-a') , \quad (\text{A15a})$$

$$\begin{aligned} \dot{\chi}(a, a', 0) &= -i \langle \delta(a-A) L \delta(a'-A) \rangle \\ &= -\frac{\partial}{\partial a} \langle \delta(a-A) \dot{A} \delta(a'-A) \rangle \\ &\equiv -\frac{\partial}{\partial a} W(a, a') . \end{aligned} \quad (\text{A15b})$$

Upon the substitution of Eqs. (A15) into Eq. (A8) we finally get the first term in the right-hand side of Eq. (30). Turning now to $\chi(a, a', \tau)$ we can trivially write

$$\chi(t) = \chi(0) + \int_0^t d\tau_1 \dot{\chi}(\tau_1) , \quad (\text{A16})$$

i. e.:

$$\chi(a, a', t) = g(a) \delta(a-a') + \int_0^t d\tau \dot{\chi}(a, a', \tau) \quad (\text{A17})$$

so that

$$\chi^{-1}(a, a', \tau) = \left[1 + \frac{1}{g(a)} \int_0^\tau d\tau_1 \dot{\chi}(\tau_1) \right]^{-1} \frac{1}{g(a')} . \quad (\text{A18})$$

When Eqs. (34) and (A18) are substituted in Eq. (A9) we finally get Eq. (33). We have added the $\sqrt{g(a')/g(a)}$ to Eq. (30) in order to make the kernel symmetric [Eq. (37)].

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