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The Linear Response Approximation and Its Lowest Order Corrections: An Influence Functional Approach

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A cumulant expansion of the influence functional entering the path integral representation of the reduced density matrix is presented. Truncation of the expansion at the quadratic terms allows mapping of a many-body environment onto an effective harmonic model with the same force autocorrelation function, recovering the conventional linear response limit. It is shown that the latter becomes exact in the thermodynamic limit if the bath consists of independent modes coupled to the system via coefficients that scale appropriately with the size of the bath. Low-order correction terms to the linear response approximation are found to be given by multitime correlation functions of the force exerted by the bath on the system. Within a classical approximation, such correction terms can be obtained from molecular dynamics calculations and incorporated in the path integral, which can be evaluated by means of iterative procedures. Numerical calculations on an intrinsically nonlinear bath of two-level systems confirm the above behaviors and indicate that the deviations from the linear response approximation are more significant at low temperatures where quantum mechanical effects play an important role to the bath dynamics.

I. Introduction

The harmonic bath model, where the degree of freedom of interest is coupled to a bath of harmonic oscillators, has served as the prototype for numerous theoretical investigations. Despite its apparent simplicity, the harmonic bath provides a robust model of condensed-phase environments by allowing for dissipative effects that lead the system to thermal equilibrium. Within the framework of classical mechanics, such effects are described by the generalized Langevin equation in which the system−bath interaction manifests itself as a frictional force that is responsible for loss.[1] Although no satisfactory quantum mechanical analogue of the Langevin equation is known, the evolution of observables pertaining to the system of interest can be obtained in terms of its reduced density matrix which is most transparently calculated via the path integral formalism[2] or, within second-order perturbation theory, via the Redfield approach.[3] In these, all features of the harmonic bath pertaining to the system of interest enter collectively via the spectral density function.

For the purpose of simulating nonglassy physical systems in the condensed phase, the harmonic bath is often deemed a reasonable approximation which can correctly capture qualitative behaviors. Recent work on inhomogeneous broadening by point defects in crystals revealed a transition from Lorentzian to Gaussian line shapes as a function of defect density.[4] It is generally understood that in some situations the true polyatomic medium can be replaced by a harmonic bath of fictitious degrees of freedom.[5−8] This equivalence, which forms the basis of Marcus' electron-transfer theory,[9] is understood to be valid *only* for the purpose of describing the dynamics of a system observable and to the extent that linear response is operative. It is not clear a priori how good this approximation is for a given

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system. Even though this question can, in principle, be addressed numerically within the classical mechanical framework,[6,10−12] the conclusions of such studies may not carry over to the quantum regime. Most importantly, no methodology is available for including corrections to the linear response approximation in a systematic fashion.

The present paper presents an influence functional approach[13] to analyze the validity of linear response theory and proposes numerical ways of including higher order corrections. The starting point is a cumulant expansion of the influence functional, which forms the basis for a justification of the linear response approximation and leads to a systematic procedure for calculating low-order anharmonic corrections. Numerical tests of the linear response approximation on an intrinsically nonlinear model bath of two-level systems are presented, which provide a quantitative feel for the accuracy of simulations based on effective harmonic baths as a function of bath size, temperature, and overall coupling strength.

The cumulant expansion of the influence functional is derived in section II. Section III discusses the truncation of that expansion at quadratic order from which the linear response approximation emerges. Practical schemes for approximating the leading order anharmonic terms are discussed in section IV. Section V presents numerical calculations of the influence functional from a two-level system bath and compares these to the predictions of the linear response approximation. Finally, some concluding remarks appear in section VI.

II. Cumulant Expansion of the Influence Functional

The effects of a bath on the dynamics of the observable system of interest are most conveniently described via the influence functional formalism. Consider a Hamiltonian for a system described by the coordinate s interacting (through potential coupling terms) with a general bath of n degrees of freedom whose coordinates are denoted collectively by the vector $\mathbf{x}$:

$$H = H_0(s, p_s) + H_b(\mathbf{x}, \mathbf{p}) + V_{\text{int}}(s, \mathbf{x}) \qquad (2.1)$$

It is assumed for simplicity that the interaction term does not depend on momentum operators and that the coupling vanishes at $s = 0$. The reduced density matrix at a time t can be expressed in terms of the path integral

$$\langle s_f | \tilde{\rho}(t) | s_0 \rangle = \int ds' \int ds'' \int \mathcal{D}s_+ \int \mathcal{D}s_- \, e^{iS_0[s_+]/\hbar}$$
$$\langle s' | \tilde{\rho}_0(t) | s'' \rangle e^{-iS_0[s_-]/\hbar} \, F[s_+, s_-] \quad (2.2)$$

Here S_0 is the action for the bare system, $\tilde{\rho}_0$ is its initial density matrix, s_+ and s_- are forward and backward paths with endpoints $\{s', s_f\}$ and $\{s'', s_0\}$, respectively, and F is the corresponding influence functional. Assuming for simplicity that the system and bath are initially uncorrelated and that the bath is described by a canonical ensemble at a temperature $1/k_B\beta$, the influence functional is given by the expression

$$F[s_+, s_-] = Z^{-1} \, \text{Tr}_b(U[s_+] \, e^{-\beta H_b} \, U^{-1} \, [s_-]) \quad (2.3a)$$

In the last equation, U is the time evolution operator that corresponds to the (time-dependent) Hamiltonian $H_b + V_{\text{int}}$ along a given system path, Z is the partition function for the isolated environment, and the trace is evaluated with respect to the bath. Note that the influence functional achieves a similar form in terms of the interaction evolution operator

$$F[s_+, s_-] = Z^{-1} \, \text{Tr}_b(U^I[s_+] \, e^{-\beta H_b} \, U^{I^{-1}} \, [s_-]) \quad (2.3b)$$

where the superscript I denotes the interaction representation with respect to the isolated bath.

Below we carry through a cumulant expansion of the influence functional; for this purpose, we write

$$F[s_+, s_-] \equiv \exp(\ln F[s_+, s_-]) \qquad (2.4)$$

and expand the exponent as follows:

$$F[s_+, s_-] =$$
$$\exp\Bigg(\int_0^t dt_1 \frac{\delta \ln F}{\delta s_+(t_1)} s_+(t_1) + \int_0^t dt_1 \frac{\delta \ln F}{\delta s_-(t_1)} s_-(t_1) +$$
$$\frac{1}{2} \int_0^t dt_1 \int_0^t dt_2 \frac{\delta^2 \ln F}{\delta s_+(t_1)\delta s_+(t_2)} s_+(t_1)s_+(t_2) +$$
$$\frac{1}{2} \int_0^t dt_1 \int_0^t dt_2 \frac{\delta^2 \ln F}{\delta s_-(t_1)\delta s_-(t_2)} s_-(t_1)s_-(t_2) +$$
$$\int_0^t dt_1 \int_0^t dt_2 \frac{\delta^2 \ln F}{\delta s_+(t_1)\delta s_-(t_2)} s_+(t_1)s_-(t_2) +$$
$$\frac{1}{3!} \int_0^t dt_1 \int_0^t dt_2 \int_0^t dt_3 \frac{\delta^3 \ln F}{\delta s_+(t_1)\delta s_+(t_2)\delta s_+(t_3)}$$
$$s_+(t_1)s_+(t_2)s_+(t_3) + ... \frac{1}{4!} \int_0^t dt_1 \int_0^t dt_2$$
$$\int_0^t dt_3 \int_0^t dt_4 \frac{\delta^4 \ln F}{\delta s_+(t_1)\delta s_+(t_2)\delta s_+(t_3)\delta s_+(t_4)}$$
$$s_+(t_1)s_+(t_2)s_+(t_3)s_+(t_4) + ... \Bigg) \quad (2.5)$$

Here the various functional derivatives are evaluated at $s_+ = s_- = 0$. Since $F[s_+ = s_- = 0] = 1$ the logarithmic derivatives are easily found to be

$$\frac{\delta \ln F}{\delta s_+(t_1)} = \frac{\delta F}{\delta s_+(t_1)} \qquad (2.6a)$$

$$\frac{\delta^2 \ln F}{\delta s_+(t_1)\delta s_+(t_2)} = -\frac{\delta F}{\delta s_+(t_1)} \frac{\delta F}{\delta s_+(t_2)} + \frac{\delta^2 F}{\delta s_+(t_1)\delta s_+(t_2)} \quad (2.6b)$$

$$\frac{\delta^3 \ln F}{\delta s_+(t_1)\delta s_+(t_2)\delta s_+(t_3)} = 2 \frac{\delta F}{\delta s_+(t_1)} \frac{\delta F}{\delta s_+(t_2)} \frac{\delta F}{\delta s_+(t_3)} -$$
$$\left(\frac{\delta^2 F}{\delta s_+(t_1)\delta s_+(t_2)} \frac{\delta F}{\delta s_+(t_3)} + \frac{\delta^2 F}{\delta s_+(t_1)\delta s_+(t_3)} \frac{\delta F}{\delta s_+(t_2)} + \right.$$
$$\left. \frac{\delta^2 F}{\delta s_+(t_2)\delta s_+(t_3)} \frac{\delta F}{\delta s_+(t_1)} \right) + \frac{\delta^3 F}{\delta s_+(t_1)\delta s_+(t_2)\delta s_+(t_3)} \quad (2.6c)$$

$$\frac{\delta^4 \ln F}{\delta s_+(t_1)\delta s_+(t_2)\delta s_+(t_3)\delta s_+(t_4)} =$$
$$-6 \frac{\delta F}{\delta s_+(t_1)} \frac{\delta F}{\delta s_+(t_2)} \frac{\delta F}{\delta s_+(t_3)} \frac{\delta F}{\delta s_+(t_4)} -$$
$$\left(\frac{\delta^2 F}{\delta s_+(t_1)\delta s_+(t_2)} \frac{\delta^2 F}{\delta s_+(t_3)\delta s_+(t_4)} + \right.$$
$$\frac{\delta^2 F}{\delta s_+(t_1)\delta s_+(t_3)} \frac{\delta^2 F}{\delta s_+(t_2)\delta s_+(t_4)} +$$
$$\left. \frac{\delta^2 F}{\delta s_+(t_1)\delta s_+(t_4)} \frac{\delta^2 F}{\delta s_+(t_2)\delta s_+(t_3)} \right) +$$

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$$2\left(\frac{\delta^2 F}{\delta s_+(t_1)\delta s_+(t_2)}\frac{\delta F}{\delta s_+(t_3)}\frac{\delta F}{\delta s_+(t_4)}+\right.$$

$$\frac{\delta^2 F}{\delta s_+(t_1)\delta s_+(t_3)}\frac{\delta F}{\delta s_+(t_2)}\frac{\delta F}{\delta s_+(t_4)}+$$

$$\frac{\delta^2 F}{\delta s_+(t_1)\delta s_+(t_4)}\frac{\delta F}{\delta s_+(t_2)}\frac{\delta F}{\delta s_+(t_3)}+$$

$$\frac{\delta^2 F}{\delta s_+(t_2)\delta s_+(t_3)}\frac{\delta F}{\delta s_+(t_1)}\frac{\delta^2 F}{\delta s_+(t_4)}+$$

$$\frac{\delta^2 F}{\delta s_+(t_2)\delta s_+(t_4)}\frac{\delta F}{\delta s_+(t_1)}\frac{\delta F}{\delta s_+(t_3)}+$$

$$\left.\frac{\delta^2 F}{\delta s_+(t_3)\delta s_+(t_4)}\frac{\delta F}{\delta s_+(t_1)}\frac{\delta F}{\delta s_+(t_2)}\right)+$$

$$\left(\frac{\delta F}{\delta s_+(t_1)}\frac{\delta^3 F}{\delta s_+(t_2)\delta s_+(t_3)\delta s_+(t_4)}+\right.$$

$$\frac{\delta F}{\delta s_+(t_2)}\frac{\delta^3 F}{\delta s_+(t_1)\delta s_+(t_3)\delta s_+(t_4)}+$$

$$\frac{\delta F}{\delta s_+(t_3)}\frac{\delta^3 F}{\delta s_+(t_1)\delta s_+(t_2)\delta s_+(t_4)}+$$

$$\left.\frac{\delta F}{\delta s_+(t_4)}\frac{\delta^3 F}{\delta s_+(t_1)\delta s_+(t_2)\delta s_+(t_3)}\right)+$$

$$\frac{\delta^4 F}{\delta s_+(t_1)\delta s_+(t_2)\delta s_+(t_3)\delta s_+(t_4)} \quad (2.6d)$$

etc.

To calculate these derivatives we express each time-evolution operator as a Dyson series in the interaction representation:

$$U^I[s_\pm] = \hat{T}\exp\left(-\frac{i}{\hbar}\int_0^t V_{\text{int}}^I(s_\pm(t'),x;t')dt'\right) \quad (2.7)$$

Again, the superscript I denotes the interaction representation with respect to the isolated bath and $\hat{T}$ is the usual time ordering operator. Substitution of the last expression in eq 2.3 leads to the following expression for the influence functional:

$$F[s_+,s_-] =$$

$$Z^{-1}\text{Tr}_b\left\{\hat{T}\exp\left(-\frac{i}{\hbar}\int_0^t V_{\text{int}}^I(s_+(t'),x;t')dt'\right)\exp(-\beta H_b)\right.$$

$$\left.\hat{T}^{-1}\exp\left(-\frac{i}{\hbar}\int_0^t V_{\text{int}}^I(s_-(t'),x;t')dt'\right)\right\} \quad (2.8)$$

Here the operator $\hat{T}^{-1}$ enforces the ascending order. Functional differentiation of the last equation and use of the cyclic property of the trace allows identification of the various functional derivatives. The first derivative terms are given by the equilibrium average

$$\frac{\delta F}{\delta s_+(t_1)} = \frac{\delta F}{\delta s_-(t_1)} = \frac{i}{\hbar}\langle f(\mathbf{x}(t_1))\rangle_\beta \quad (2.9)$$

where

$$f(\mathbf{x}(t_1)) \equiv -e^{iH_bt_1/\hbar}\frac{\partial V_{\text{int}}(s,\mathbf{x})}{\partial s}\bigg|_{s=0}e^{-iH_bt_1/\hbar} \quad (2.10)$$

is the force exerted on the system due to its interaction with the bath $\langle\cdots\rangle_\beta$ and denotes the equilibrium average with respect to the isolated environment. The second functional derivatives involve the force autocorrelation function and are given by the

relations

$$\frac{\delta^2 F}{\delta s_+(t_1)\delta s_+(t_2)} = -\frac{1}{\hbar^2}\langle f(\mathbf{x}(t_>))f(\mathbf{x}(t_<))\rangle_\beta \quad (2.11a)$$

$$\frac{\delta^2 F}{\delta s_-(t_1)\delta s_-(t_2)} = -\frac{1}{\hbar^2}\langle f(\mathbf{x}(t_>))f(\mathbf{x}(t_<))\rangle_\beta^* \quad (2.11b)$$

$$\frac{\delta^2 F}{\delta s_+(t_1)\delta s_-(t_2)} = \frac{1}{\hbar^2}\langle f(\mathbf{x}(t_1))f(\mathbf{x}(t_2))\rangle_\beta^* \quad (2.11c)$$

Here $t_>$ and $t_<$ are the larger and smaller of the times t_1 and t_2, respectively.

The third-order terms are found to be given for $t_1 \geq t_2 \geq t_3$ by the expressions

$$\frac{\delta^3 F}{\delta s_+(t_1)\delta s_+(t_2)\delta s_+(t_3)} = -\frac{1}{\hbar^3}\langle f(\mathbf{x}(t_1))f(\mathbf{x}(t_2))f(\mathbf{x}(t_3))\rangle_\beta \quad (2.12a)$$

$$\frac{\delta^3 F}{\delta s_+(t_1)\delta s_+(t_2)\delta s_-(t_3)} = \frac{1}{\hbar^3}\langle f(\mathbf{x}(t_3))f(\mathbf{x}(t_1))f(\mathbf{x}(t_2))\rangle_\beta \quad (2.12b)$$

$$\frac{\delta^3 F}{\delta s_+(t_1)\delta s_-(t_2)\delta s_-(t_3)} = \frac{1}{\hbar^3}\langle f(\mathbf{x}(t_2))f(\mathbf{x}(t_3))f(\mathbf{x}(t_1))\rangle_\beta \quad (2.12c)$$

$$\frac{\delta^3 F}{\delta s_-(t_1)\delta s_-(t_2)\delta s_-(t_3)} = \frac{1}{\hbar^3}\langle f(\mathbf{x}(t_3))f(\mathbf{x}(t_2))f(\mathbf{x}(t_1))\rangle_\beta \quad (2.12d)$$

while the fourth-order terms are given by four time correlation functions.

Evidently, the lowest order terms which survive will dominate in the above expansion if the system−bath coupling is sufficiently weak. This is the case if the system−bath interaction is diluted uniformly over a large number of degrees of freedom. A typical example is offered by separable baths of the type employed in the spin−boson model which are representative of lattice phonons. Another example is that of electronically nonadiabatic transitions if the latter are accompanied by a rearrangement of a large number of solvent coordinates. This situation is discussed further in the next section.

III. Linear Response and Effective Harmonic Bath

In the first part of this section we show that the linear response approximation is exact in the thermodynamic limit if the bath is composed of independent degrees of freedom, i.e., if

$$H_b = \sum_{i=1}^n H_i, \quad V_{\text{int}} = -\varphi(s)\sum_{i=1}^n c_i g(x_i) \quad (3.1)$$

where $\varphi'(0) \neq 0$ and g is an unspecified function. Further, we assume $\varphi'(0) = 1$ without loss of generality. In this case, the force due to the bath is

$$f(\mathbf{x}(t)) = \sum_{i=1}^n c_i g(x_i(t)) \quad (3.2)$$

The first-order term in the cumulant expansion of the influence functional involves the ensemble average of the force exerted on the system, which is time-independent. This term often vanishes because of symmetry. Nonetheless, if the average

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force is *not* equal to zero, Suarez and Silbey have argued[14] that the couplings must scale as $c_i \propto 1/n$. Examining the quadratic terms, one observes that

$$\sum_{i=1}^{n}\sum_{j=1}^{n} c_i c_j \langle g(x_i(t_1))g(x_j(t_2))\rangle_\beta =$$
$$\sum_{i=1}^{n} c_i^2 \langle g(x_i(t_1))g(x_i(t_2))\rangle_\beta + \sum_{i=1}^{n}\sum_{j\neq i} c_i c_j \langle g(x_i(t_1))\rangle_\beta \langle g(x_j(t_2))\rangle_\beta$$

$$(3.3a)$$

The first of these terms vanishes in the $n \to \infty$ limit, and therefore, by virtue of eq 2.6b, it follows that $\delta^2 \ln F/\delta s_+(t_1)\delta s_+(t_2) = 0$. Higher order correlation functions produce multiple terms when decomposed this way, e.g.,

$$\sum_{i=1}^{n}\sum_{j=1}^{n}\sum_{k=1}^{n} c_i c_j c_k \{\langle g(x_i(t_1))\rangle\langle g(x_j(t_2))g(x_k(t_3))\rangle_\beta +$$
$$\langle g(x_i(t_2))\rangle\langle g(x_j(t_1))g(x_k(t_3))\rangle_\beta +$$
$$\langle g(x_i(t_3))\rangle\langle g(x_j(t_1))g(x_k(t_2))\rangle_\beta \underset{n\to\infty}{=}$$
$$3\sum_{i\neq j\neq k} \langle g(x_i(t_1))\rangle\langle g(x_j(t_2))\rangle g(x_k(t_3))\rangle \quad (3.3b)$$

By taking into account the multiplicity of such correlation functions, one can show that *all* higher order terms also drop out in the infinite dimension limit and the influence functional is governed by a static property of the bath.

In many situations, the average force exerted on the system is identically equal to zero while the variance of the force is finite. Under such conditions (and assuming that the coupling coefficients do not depend on other parameters such as a radial distance), it follows[14] that the coupling coefficients scale as $c_j \propto 1/\sqrt{n}$. This scaling can be derived from first principles in the case of the interaction between an impurity and the phonon modes of a crystalline solid. From eqs 2.6b and 3.3, this scaling implies that

$$\frac{\delta^2 \ln F}{\delta s_+(t_1)\delta s_+(t_2)} = -\hbar^{-2}\sum_{i=1}^{n} c_i^2 \langle g(x_i(t_>))g(x_i(t_<))\rangle_\beta \quad (3.4)$$

while use of eq 2.6c leads immediately to the conclusion $\delta^2 \ln F/\delta s_+(t_1)\delta s_+(t_2)\delta s_+(t_3) = 0$. Proceeding as in the case of nonzero mean force, we observe that fourth-order terms vanish in the limit $n \to \infty$ unless they can be reduced to double sums of the type

$$\sum_{i=1}^{n}\sum_{j=1}^{n} c_i^2 \, c_j^2 \langle g(x_i(t_1))g(x_i(t_2))\rangle_\beta \langle g(x_j(t_3))g(x_j(t_4))\rangle_\beta \quad (3.5)$$

Once again, all such terms entering eq 2.6d sum to zero, implying that the terms of fourth order in the system−bath interaction vanish in the thermodynamic limit. Using similar arguments, it can be shown that all terms higher than second-order vanish for $n \to \infty$, such that the influence functional assumes a Gaussian form. This result holds irrespective of the specific form of the bath operators in eq 3.1.

In the special case of an *n*-dimensional harmonic bath coupled bilinearly to the system

$$H_b = \sum_{i=1}^{n} \frac{p_i^2}{2m_i} + \frac{1}{2} m_i \omega_i^2 x_i^2, \qquad V_{\text{int}} = -s\sum_{i=1}^{n} c_i x_i \quad (3.6)$$

the linear terms vanish, while an elementary calculation gives the force autocorrelation function as

$$\langle f(\mathbf{x}(t_1))f(\mathbf{x}(t_2))\rangle_\beta = \sum_{i=1}^{n} c_i^2 \langle x_i(t_1)x_i(t_2)\rangle_\beta \quad (3.7)$$
$$= \frac{\hbar}{\pi}\int_0^\infty J(\omega)\left(\coth\left(\frac{1}{2}\hbar\omega\beta\right)\cos\omega(t_1-t_2) - i\sin\omega(t_1-t_2)\right)d\omega \quad (3.7)$$

where the discrete sum has been replaced by an integral employing the spectral density function,

$$J(\omega) = \frac{\pi}{2}\sum_{i=1}^{n} \frac{c_i^2}{m_i\omega_i}\delta(\omega-\omega_i) \quad (3.8)$$

Using these results one recovers the influence functional expression obtained by Feynman and Vernon.[13]

Now we assume that linear response is valid in a given physical situation, i.e., that the third-order term in the influence functional is negligible. According to the analysis given above, this condition is guaranteed if the system−bath coupling is distributed uniformly over a practically infinite number of degrees of freedom, as in the case of an impurity interacting with the acoustic phonons of a lattice, but may also represent a reasonable approximation in other situations. Recalling that the terms of second order in the system−bath coupling involve the force−force autocorrelation function of the medium

$$C_2(t') \equiv \langle f(\mathbf{x}(0))f(\mathbf{x}(t'))\rangle_\beta \quad (3.9)$$

it is straightforward to construct an *effective* harmonic bath whose correlation function is the same as that of the nonlinear medium at hand at the given temperature. Specifically, this procedure has been used by several workers (see, for example, refs 6, 11, 22). Specifically, one inverts the available correlation function of the true bath to obtain the spectral density of the effective harmonic modes; from eq 3.7

$$J_{\text{eff}}(\omega,\beta) = \frac{2}{\hbar}\tanh\left(\frac{1}{2}\hbar\omega\beta\right)\int_0^\infty \text{Re }C_2(t)\cos\omega t\, dt \quad (3.10)$$

Note that only the real part of the correlation function enters the transformation of eq 3.10. This observation is important because it allows construction of an approximate effective spectral density from knowledge of the *classical* correlation function, which is more likely to be available for a given polyatomic medium. It is easy to show that the correlation function of the effective harmonic bath constructed according to eq 3.10 will necessarily be identical to that of the actual nonlinear bath, and thus no information has been lost. The equality of the imaginary components follows from the Kramers−Kronig relations which connect the real and imaginary parts of a correlation function. In practice, one obtains the classical limit of the correlation function via a molecular dynamics simulation and uses the classical limit of the above correspondence to extract the effective spectral density. Note that the latter is generally temperature dependent.

It should be emphasized that the coordinates of the harmonic modes that constitute the fictitious bath are *not* necessarily

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related to instantaneous normal modes of a fluid. When the motion is very anharmonic, the correlation function can differ dramatically from that corresponding to the quadratic expansion of the potential about a local minimum. The transformation of eq 3.10 then picks modes with frequencies similar to those present in the correlation function, which may be dominated by motions in the highly excited, anharmonic region of the multidimensional potential. Further, in contrast to the instantaneous normal modes of a fluid, the effective harmonic bath has only real-valued frequencies.

In a recent article,[15] Cao and Voth also described an optimized quadratic approximation to thermodynamic quantities or correlation functions. The main result of that work is the construction of an effective quadratic potential from the zero-time limit of the force−force correlation function of the medium, whose frequencies are extracted self-consistently via a normal-mode transformation. The effective harmonic bath defined by eq 3.10 in this paper is generally quite different, as it is designed to mimic the *dynamical* behavior of the environment. In addition, in contrast to the results of ref 15 where the nonlinear equations obtained may have multiple solutions, eq 3.10 of the present article leads to a unique definition of the spectral density.

IV. Higher Order Corrections

Using the results of section II, one can (with modest effort) calculate low-order anharmonic terms that constitute corrections to the linear response approximation. To include third-order terms, one needs (in addition to the equilibrium average and the autocorrelation function of the force) the three-point correlation function of the bath

$$C_3(t_1, t_2) \equiv \langle f(\mathbf{x}(0))f(\mathbf{x}(t_1))f(\mathbf{x}(t_2))\rangle_\beta \qquad (4.1)$$

The classical limit of this function can be obtained from molecular dynamics simulations. From this, one can infer the corresponding imaginary part by invoking Kramers−Kronig-type relations, thus reconstructing the correlation function (within the accuracy of a classical simulation). It is generally not possible to devise a simple effective bath that matches this correlation function, but this is hardly necessary since the obtained three-point correlation function can be substituted directly in the influence functional. This procedure can be used as a practical check of accuracy for the linear response approximation and can (if the perturbation series converges rapidly) yield important corrections to the latter.

Numerical evaluation of the path integral requires discretization of the paths. Use of a time step $\Delta t = t/N$ and factorization of the time evolution operator for a sufficiently large value of N leads to the following discretized path integral expression for the reduced density matrix

$$\tilde{\rho}(s'', s'; N\Delta t) =$$
$$\int ds_0^+ \int ds_1^+ \cdots \int ds_{N-1}^+ \int ds_0^- \int ds_1^- \cdots$$
$$\int ds_{N-1}^- \langle s''|e^{-iH_0\Delta t/\hbar}|s_{N-1}^+\rangle$$
$$\langle s_{N-1}^+|e^{-iH_0\Delta t/\hbar}|s_{N-2}^+\rangle \cdots \langle s_1^+|e^{-iH_0\Delta t/\hbar}|s_0^+\rangle \langle s_0^+|\rho_s(0)|s_0^-\rangle$$
$$\langle s_0^-|e^{iH_0\Delta t/\hbar}|s_1^-\rangle\langle s_1^-|e^{iH_0\Delta t/\hbar}|s_2^-\rangle \cdots \langle s_{N-1}^-|e^{iH_0\Delta t/\hbar}|s'\rangle$$
$$F(s_0^+,s_1^+,...s_N^+,s_0^-,s_1^-,...s_N^-) \quad (4.2)$$

where the influence functional through third order in the cumulant expansion is

$$F(s_0^+,s_1^+,...s_N^+,s_0^-,s_1^-,...s_N^-) =$$
$$\exp\{-\sum_{k=0}^N (\zeta_k^+ s_k^+ + \zeta_k^- s_k^-) -$$
$$\sum_{k=0}^N \sum_{k'=0}^N (\eta_{kk'}^{++} s_k^+ s_{k'}^+ + \eta_{kk'}^{+-} s_k^+ s_{k'}^- + \cdots) -$$
$$\sum_{k=0}^N \sum_{k'=0}^N \sum_{k''=0}^N (\theta_{kk'k''}^{+++} s_k^+ s_{k'}^+ s_{k''}^+ + \theta_{kk'k''}^{++-} s_k^+ s_{k'}^+ s_{k''}^- + \cdots) - \cdots\}$$
$$(4.3)$$

Here the coefficients ζ_k, $\eta_{kk'}$ and $\theta_{kk'k''}$ are the discrete time analogues of the force moments defined above. Equation 4.3 can be simplified by making use of symmetry properties of the bath correlation functions.

Global summation of the path integral is straightforward in principle. However, it is not practical for long times because the number of terms to be summed grows exponentially with the number of time steps. Nevertheless, just as in the case of a harmonic bath,[16−18] it is possible to replace the global summation over paths by an iterative procedure if the bath correlation functions decay to zero within a time interval which is in practice finite. Given the systematic expansion of eq 4.3, it is a straightforward extension of the theory presented in refs 16−18 to construct a propagator tensor or functional of statistically significant path segments which can be used to propagate the reduced density matrix iteratively, allowing calculation of the system dynamics for very long time intervals.

V. Numerical Test: The Two-Level System Bath

To provide a quantitative feel for the accuracy of the linear response approximation, this section presents numerical calculations of the influence functional in the case where the bath consists of a collection of two-level systems (TLS). This particular model is chosen because of its intrinsic nonlinearity and also because its correlation function is available in closed form. The Hamiltonian is

$$H_b = -\frac{1}{2}\hbar \sum_{i=1}^n \omega_i \sigma_x^i \qquad (5.1)$$

while the system−bath interaction is bilinear

$$V_{int} = -\sigma_z^0 \sum_{i=1}^n c_i \sigma_z^i \qquad (5.2)$$

Here σ_x and σ_z are the usual Pauli spin operators. The force function entering the influence functional is now

$$f(\mathbf{x}(t')) = \sum_{i=1}^n c_i \sigma_z^i(t') \qquad (5.3)$$

The average of this force is identically equal to zero, while its autocorrelation function is given by the expression

$$\langle f(\mathbf{x}(t'))f(\mathbf{x}(t''))\rangle_\beta =$$
$$\frac{\hbar}{\pi} \int_0^\infty J(\omega)\Big(\cos \omega(t' - t'') - i \tanh\Big(\frac{1}{2}\hbar\omega\beta\Big) \sin \omega(t' - t'')\Big)d\omega$$
$$(5.4)$$

From these equations one recovers immediately the result of Caldeira et al.[19] (which was obtained by expanding the influence functional to second order and re-exponentiating the result)
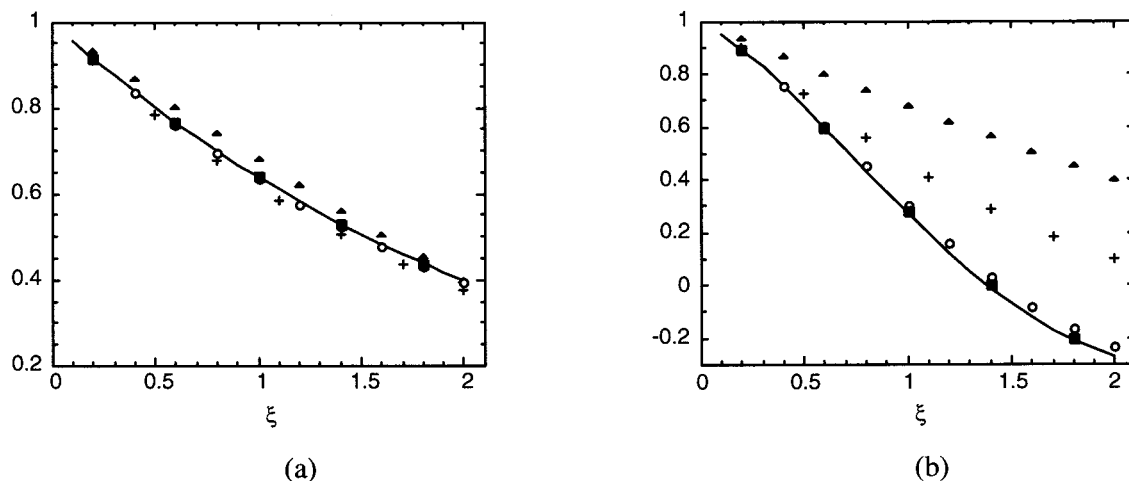
Figure 1. Real part of the influence functional for a TLS bath as a function of the Kondo parameter. ($\triangle$) $n = 1$. ($+$) $n = 10$. ($\bigcirc$) $n = 50$. Solid squares: $n=200$. The solid line shows the results obtained from an effective harmonic bath with the spectral density given in eq 3.3. (a) High temperature, $\hbar\omega_c\beta = 0.3$. (b) Low temperature, $\hbar\omega_c\beta = 15$.

where the two-level system bath is mapped onto a harmonic bath with an effective spectral density given by

$$J_{\text{eff}}(\omega,\beta) = \coth\left(\frac{1}{2}\hbar\omega\beta\right) J(\omega) \qquad (5.5)$$

Numerical evaluation of the two-level system influence functional requires discretization of the spectrum. Rather than choosing the TLS frequencies uniformly, a physically meaningful discretization is employed here, which assumes a density of states for the bath that scales as in the Debye theory of solids. Namely, the integrated density of states up to the frequency ω_j of the jth bath degree of freedom is set equal to j. Choosing an Ohmic model for the spectral density

$$J(\omega) = \frac{1}{2}\pi\hbar\xi\,\omega\,e^{-\omega/\omega_c} \qquad (5.6)$$

where ξ is the Kondo parameter, and setting the density of states

$$d(\omega) = \omega_0^{-1}\,e^{-\omega/\omega_c} \sim J(\omega)/\omega \qquad (5.7)$$

this procedure leads to the relation

$$\omega_j = -\omega_c\,\ln\left(1 - j\frac{\omega_0}{\omega_c}\right) \qquad (5.8)$$

Next, use of the density of states $d(\omega)$ in place of the delta function in eq 3.8

$$J(\omega) = \frac{\pi}{2}\sum_{i=1}^{n}\frac{c_i^2}{m_i\omega_i}\,d(\omega_i) \qquad (5.9)$$

determines the coupling coefficients as

$$c_i = \sqrt{\xi\hbar\omega_0 m_i}\,\omega_i \qquad (5.10)$$

Finally, requiring that the integral of $d(\omega)$ up to a chosen maximum discretization frequency ω_{max} should equal the total number n of bath modes allows determination of the normalization constant

$$\omega_0 = \frac{\omega_c}{n}(1 - e^{-\omega_{\text{max}}/\omega_c}) \qquad (5.11)$$

Equations 5.8, 5.10, and 5.11, completely determine the parameters of the discretized bath. This discretization of the spectral density leads to rapid convergence of the results with the number n of explicit bath degrees of freedom.

The influence functional of a separable bath can be calculated without resorting to approximations by expressing it as a product of one-dimensional factors. Following the procedure developed by Ilk and Makri,[20] the influence functional for a given discretized path of the coupled system is calculated numerically by matrix multiplication of the relevant propagators and density matrix. Results are presented below for a system path (chosen arbitrarily) of length equal to 6.75 ω_c^{-1} as a function of the number of TLS degrees of freedom, the temperature, and the Kondo parameter.

Figure 1 shows the real part of the influence functional as a function of the Kondo parameter for a TLS bath discretized in terms of 1, 10, 50, and 200 degrees of freedom and compares to the influence functional from an effective harmonic bath whose spectral density is given by eq 5.5. The deviations from the results of the effective harmonic model increase with increasing ξ. Figure 2 shows the influence functional as a function of the number n of bath degrees of freedom for a fixed ξ. For a given value of the Kondo parameter, increasing the number n of bath degrees of freedom leads to a decrease in the coupling constant of each TLS, resulting in smaller deviations from the results of the linear response approximation. In agreement with the analysis given in the previous section, the results of the effective harmonic model become exact in the infinite dimension limit. However, the convergence is seen to be much slower if the temperature of the bath is low, in agreement with the conclusions reached by Onuchic and Wolynes.[7] Clearly, the anharmonic nature of the bath is felt by the system more strongly at low temperatures, and it takes a larger number of bath degrees of freedom to dilute the coupling in order to observe linear response in that case. Nevertheless, it is seen that the numerical results become indistinguishable from those of the effective harmonic bath for *any* value of the system−bath coupling strength ξ if the number n of discrete modes is chosen sufficiently large.

VI. Concluding Remarks

This paper presents an influence functional approach to the study of the linear response approximation and its lowest order corrections. A cumulant expansion of the influence functional
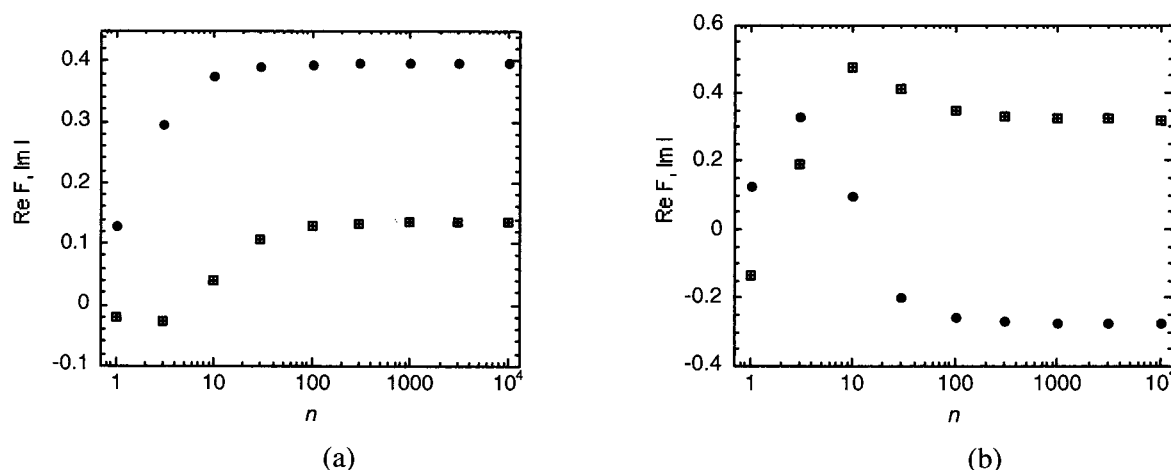
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Figure 2. The influence functional for a TLS bath as a function of the number of TLS degrees of freedom for $\xi = 2$. (O) real part. (⊞) imaginary part. (a) High temperature, $\hbar\omega_c\beta = 0.3$. (b) Low temperature, $\hbar\omega_c\beta = 15$.

arising from an arbitrary bath interacting with a general one-dimensional system was obtained in which the coefficient of the kth term is given by the k-point correlation function of the force exerted on the system. This structure of the influence functional is reminiscent of the correlation function formalism for molecular spectroscopy, where the "bath" is the electromagnetic radiation field. In that theory, the linear response limit corresponds to the dipole moment correlation function while nonlinear measurements are governed by higher order moments.[21]

Truncation of the expansion at the second-order term maps the nonlinear bath onto an effective harmonic one with a temperature-dependent spectral density which can be inferred from the classical force autocorrelation function. This truncation, usually referred to as the linear response approximation, is exact if the system–bath coupling is spread uniformly over an infinite number of bath degrees of freedom, as in the case of a separable bath.

Perhaps the most common physical situation that illustrates such behavior is the process of electron transfer in solution or in a large biological molecule which has been discussed extensively in the literature. The dynamics of such a process are governed by the characteristics of the nuclear degrees of freedom for each charge state and the statistics of their fluctuations during charge transfer. If the transfer is accompanied by rearrangement of a large number of atoms, the reorganization energy will be spread over a large number of coordinates and the resulting coupling to each nuclear coordinate will be small. In that case, the nuclear coordinates will exhibit linear response and the free energy surfaces will be nearly parabolic. Deviations from this behavior are expected if some degrees of freedom are affected more strongly, such that their couplings are large compared to the average coupling of the other bath modes. As seen from the numerical calculations of section V, deviations from linear response are in general larger at lower temperatures.

Finally, it was shown that low-order corrections to the linear response approximation can indeed be calculated and incorporated into an iterative procedure for evaluating the path integral. Approximate extraction of the necessary influence functional

coefficients from classical trajectory simulations appears possible by virtue of the Kramers–Kronig relations. Estimates of the lowest order anharmonic terms may be valuable in assessing the extent of validity of the effective harmonic bath model for a given process. In addition, inclusion of these terms in a numerical calculation will lead to quantitative results if the deviations from linear response are small, in which case the cumulant expansion is expected to converge rapidly.

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