Evaluation of Quantum Correlation Functions from Classical Data[†]

Hyojoon Kim and Peter J. Rossky*

Institute for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712

Received: March 11, 2002; In Final Form: May 14, 2002

The general problem of evaluating quantum mechanical time correlation functions of quantities that are functions of condensed phase bath coordinates is addressed. On the basis of the relation between such a general correlation function and that for the position variable, and the analytical result for the relation of quantum and classical correlation functions of position for harmonic baths, we develop an approximate expression for the quantum correction to the general classical correlation function as an expansion in the quantum correction. The quantum corrected correlation function only requires classical correlation functions and their derivatives with respect to time and temperature. Hence, the result can be implemented directly using only computer simulated classical data. Application to analytically solved model problems involving harmonic baths demonstrates that the method is accurate both for highly nonlinear coupling and surprisingly small temperature.

I. Introduction

It is well established that many experimental phenomena can be described effectively theoretically by expressions that are formulated in terms of appropriate time correlation functions (CFs) of dynamical variables. The calculation of classical time CFs from molecular dynamics simulations in the condensed phase is also well established. The difficulty arises in systems where significant quantum effects occur because fully quantum simulations for systems with large numbers of degrees of freedom remain inaccessible, despite the growth of computational power. The main interest in such systems is typically one involving an interesting subsystem in a condensed phase bath, such as a solvent. Because the bath molecules correspond to the vast majority of degrees of freedom, mixed quantum-classical methods, which treat the sub-system quantum mechanically and bath molecules classically, are an attractive alternative. However, recent progress, particularly focused in the area of vibrational relaxation, has demonstrated that bath quantum effects can be very large, and that, in some cases, the mixed quantum-classical approach can yield results far less accurate than a completely classical treatment of both bath and solute.[1,2]

If one can find a useful relationship between the classical and quantum CF, one can calculate quantum effects using classical, or potentially mixed quantum-classical, methods. Obtaining an accessible relationship is the main purpose of this paper. To this end, we focus on the context of vibrational energy relaxation in the present paper, although the results are developed in somewhat greater generality. The vibrational energy relaxation of molecules in condensed phases plays an essential role in a wide variety of chemical and biochemical processes.[3−8] Besides its practical importance, it is also an excellent theoretical subject in the present context because Fermi's golden rule provides us with a simple formula for the transition rate between solute vibrational states $|n\rangle$ and $|m\rangle$ in terms of a correlation function of bath coordinates, namely[3]

$$k_{nm} = \frac{|x_{nm}|^2}{\hbar^2}\int_{-\infty}^{\infty} dt\, \exp(i\omega_{nm}t)\langle F(t)F(0)\rangle_{qm} \tag{1}$$

where $x_{nm} = \langle n|x|m\rangle_{qm}$, x is a solute vibrational coordinate of interest, ω_{nm} the frequency corresponding to the energy difference between states, F the force exerted by the bath on the coordinate x, and $\langle ...\rangle_{qm}$ denotes a trace over the quantum bath states. Note that the force is a function of collective bath coordinates q. If q is effectively the same as a coordinate operator for a harmonic potential, then the bath is a harmonic bath. Hence, the problem of determining the vibrational transition rate reduces to that of obtaining the force-force CF quantum mechanically.

The approach followed for many years, sometimes referred to as the "standard" approach, involves the replacement of the real part of the quantum correlation function by the classical analog.[3] With this assumption, the rate constant of eq 1 can be expressed exactly as

$$k_{nm} = \frac{|x_{nm}|^2}{\hbar^2}\frac{2}{1+\exp(-\beta\hbar\omega_{nm})}\int_{-\infty}^{\infty} dt\, \exp(i\omega_{nm}t)\langle F(t)F(0)\rangle_{cl}. \tag{2}$$

More recent work has shown that this assumption is not broadly applicable. In particular, Bader and Berne[1] found that the following relation holds between the Fourier transform of the classical CF for linear coupling and that of quantum CF, a result that is exact for harmonic baths[9]

$$\int_{-\infty}^{\infty} dt e^{i\omega t}\langle [q(t),q(0)]_+/2\rangle_{qm} = \frac{\beta\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right)\int_{-\infty}^{\infty} dt e^{i\omega t}\langle q(t)q(0)\rangle_{cl}, \tag{3}$$

where $[A,B]_+ = AB + BA$ is the anticommutor. The quantum CF can be easily obtained in this case, simply by multiplying the classical CF by a so-called quantum correction factor. Because such a quantum correction approach is quite appealing,

---

[†] Part of the special issue "John C. Tully Festschrift".

10.1021/jp020669n CCC: $22.00

there have been efforts to find a more general quantum correction factor for general coupling.[10−12] Egorov et al.[11] critically reviewed the known quantum correction approaches which include standard,[3,13] harmonic,[1,14] Schofield,[15] and Egelstaff[16] approximations. By comparing the results of these approaches for exactly solvable models, they found that no method was satisfactory for all of the models they considered, and, more importantly, the performance was inconsistent and evidently unpredictable. Thus, the process of estimating these quantum correlation functions for complex systems was not controlled. Further, the method that appeared to perform overall most accurately, the Egelstaff[16] approximation, requires the evaluation of the classical correlation function at a complex argument. Hence, either a functional form is required for the CF or one must accurately evaluate a numerical Fourier transform and an inverse Fourier transform. The same complication is associated with the Schofield[15] approach.

This situation motivated us to pursue a more reliable method to calculate general quantum CFs. In the present paper, we consider a fairly general CF between functions of bath coordinates. We focus on the development of the quantum correction to the general CF in terms of the quantum correction, denoted Q, for the linear autocorrelation function of position itself. Using the exact result for the correction Q for a harmonic bath, and expanding the correction to the general CF in terms of Q, we obtain an explicit expression for the general CF in terms of classical CFs and their time derivatives. We test our new result for two exactly solvable harmonic models that have been considered by others, and demonstrate its usefulness. In the following section, we outline the derivation of the method. The numerical results and comparison with other methods are presented and discussed in section III, followed by concluding remarks in section IV.

II. Theory

In this section, we utilize a previously developed expansion[17] of a general CF in terms of the linear position CF to develop an expression for a generally applicable time domain quantum CF approximation.

A. Development of the CF in the Time Domain. We start by defining the following general time CF

$$G_{qm}(t) \equiv \langle f(t)g(0)\rangle_{qm}, \tag{4}$$

$$G_{cl}(t) \equiv \langle f(t)g(0)\rangle_{cl}, \tag{5}$$

where f and g are assumed as functions of a collective bath coordinate q. $\langle ...\rangle_{qm}$ and $\langle ...\rangle_{cl}$ are traces over the quantum and classic bath states, respectively. If the functions are equal to q, i.e., $f = g = q$, the CF becomes the linear position CF, denoted hereafter as $C(t)$, namely

$$C_{qm}(t) \equiv \langle q(t)q(0)\rangle_{qm} \tag{6}$$

and its classic analogue $C_{cl}(t)$.

When the bath is taken to be harmonic, one can evaluate $C(t)$ exactly[11]

$$C_{qm}(t) = \hbar\int_0^{\infty} d\omega J(\omega)\{\coth(\beta\hbar\omega/2)\cos\omega t - i\sin\omega t\}, \tag{7}$$

$$C_{cl}(t) = \int_0^{\infty} d\omega J(\omega)\frac{2}{\beta\omega}\cos\omega t, \tag{8}$$

defined in terms of the bath spectral density $J(\omega) = \sum_k c_k^2\delta(\omega - \omega_k)$ with the real expansion coefficients c_k. Then a close comparison of eqs 7 and 8 leads to the relation between $C_{qm}(t)$ and $C_{cl}(t)$

$$\begin{aligned} C_{qm}(t) &= C_{cl}(t) + \frac{i\beta\hbar}{2}\frac{d}{dt}C_{cl}(t) + \frac{(i\beta\hbar)^2}{12}\frac{d^2}{dt^2}C_{cl}(t) + ... \\ &= \sum_{n=0}^{\infty}\frac{-(\beta\hbar)^{2n}B_n}{(2n)!}\left(\frac{d}{dt}\right)^{2n}C_{cl}(t) + \frac{i\beta\hbar}{2}\frac{d}{dt}C_{cl}(t) \\ &= \frac{i\beta\hbar(d/dt)}{1-\exp\{-i\beta\hbar(d/dt)\}}C_{cl}(t) \end{aligned} \tag{9}$$

where B_n is Bernoulli number, and the exponential of an operator is defined in the usual way. This relation holds for any spectral density. With the Fourier transform $\tilde{C}_{qm}(\omega) \equiv \int_{-\infty}^{\infty} dt \exp(i\omega t) C_{qm}(t)$, we can recover the relation obtained by Bader and Berne[1] in frequency space

$$\tilde{C}_{qm}(\omega) = \frac{\beta\hbar\omega}{1-\exp(-\beta\hbar\omega)}\tilde{C}_{cl}(\omega) = \left\{\frac{\beta\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right) + \frac{\beta\hbar\omega}{2}\right\}\tilde{C}_{cl}(\omega) \tag{10}$$

The second term on the right in eq 10 emerges since the CF here is not symmetrized (cf., eq 3). As for the relation in eq 3, eq 10 is particularly useful because the quantum CF can be obtained simply by multiplying the classical CF by a correction factor. To get the value of $C_{qm}(t)$ from $C_{cl}(t)$, one can take advantage of either the expansion of eq 9 or the inverse Fourier transform of eq 10.

To find the relation between $G_{qm}(t)$ and $G_{cl}(t)$, we rewrite the general CF, eq 4, following Egorov and Skinner.[17] One uses the general identity

$$\langle f\{q(t)\}g\{q(0)\}\rangle = \langle \exp\{q(t)(\partial/\partial q')\}\exp\{q(0)(\partial/\partial q'')\}f(q')g(q'')\rangle_{q'=0,q''=0} \tag{11}$$

and we make the assumption of a harmonic bath, for which one has the identity $\langle\exp(A)\rangle = \exp[\langle A^2\rangle/2]$ yielding

$$\begin{aligned} &\langle\exp\{q(t)(\partial/\partial q')\}\exp\{q(0)(\partial/\partial q'')\}\rangle \\ &= \exp\{C(0)/2(\partial^2/\partial q'^2)\}\exp\{C(0)/2(\partial^2/\partial q''^2)\}\exp\{C(t)(\partial^2/\partial q'\partial q'')\} \end{aligned} \tag{12}$$

Thus, they found

$$G_{qm}(t) = \sum_{k,l,m}\frac{C_{qm}(0)^{l+m}C_{qm}(t)^k}{k!l!m!2^{l+m}}f_{2l+k}g_{2m+k}, \tag{13}$$

where $f_n \equiv d^n f(q)/dq^n|_{q=0}$ and $g_n \equiv d^n g(q)/dq^n|_{q=0}$. This equation demonstrates that, for a harmonic bath, the general CF can be represented in terms of the linear CF, for which we already know the relation between quantum and classical CF. The classical CF can be expressed similarly

$$G_{cl}(t) = \sum_{k,l,m}\frac{C_{cl}(0)^{l+m}C_{cl}(t)^k}{k!l!m!2^{l+m}}f_{2l+k}g_{2m+k}. \tag{14}$$

Defining the quantum correction to $C(t)$ as $Q(t)$

$$Q(t) = C_{qm}(t) - C_{cl}(t) \tag{15}$$

we utilize a binomial expansion as follows

$$C_{qm}(t)^k = C_{cl}(t)^k + kC_{cl}(t)^{k-1}Q(t) + \frac{k(k-1)}{2}C_{cl}(t)^{k-2}Q(t)^2 + ...$$

$$= \exp\{Q(t)\partial/\partial C_{cl}(t)\}C_{cl}(t)^k \tag{16}$$

When we use eq 16 to substitute for $C_{qm}(t)^k$ and $C_{qm}(0)^{l+m}$ in eq 13, we obtain the following relation

$$G_{qm}(t) = \sum_{k,l,m}\frac{f_{2m+k}g_{2l+k}}{l!m!2^{l+m}k!}\exp[\{Q(0)\partial/\partial C_{cl}(0)\}_{C_{cl}(t)}]C_{cl}(0)^{l+m}$$

$$\times \exp[\{Q(t)\partial/\partial C_{cl}(t)\}_{C_{cl}(0)}]C_{cl}(t)^k \tag{17}$$

$$= \exp[\{Q(0)\partial/\partial C_{cl}(0)\}_{C_{cl}(t)} + \{Q(t)\partial/\partial C_{cl}(t)\}_{C_{cl}(0)}]G_{cl}(t)$$

This is an exact expression within the harmonic bath assumption and is one of the main results of the present paper. It can be expanded in various ways. One can easily confirm that eq 17 holds for two model cases $G_{cl}(t) = C_{cl}(t)$ and $G_{cl}(t) = e^{C_{cl}(0)}\{e^{C_{cl}(t)} - 1\}$.

The last equation can be expanded in Q as

$$G_{qm}(t) = G_{cl}(t) + Q(t)\left(\frac{\partial G_{cl}(t)}{\partial C_{cl}(t)}\right)_{C_{cl}(0)} + Q(0)\left(\frac{\partial G_{cl}(t)}{\partial C_{cl}(0)}\right)_{C_{cl}(t)} + \frac{Q(t)^2}{2}\left(\frac{\partial^2 G_{cl}(t)}{\partial C_{cl}(t)^2}\right)_{C_{cl}(0)}$$

$$+ Q(t)Q(0)\left(\frac{\partial}{\partial C_{cl}(t)}\right)_{C_{cl}(0)}\left(\frac{\partial}{\partial C_{cl}(0)}\right)_{C_{cl}(t)} G_{cl}(t) + \frac{Q(0)^2}{2}\left(\frac{\partial^2 G_{cl}(t)}{\partial C_{cl}(0)^2}\right)_{C_{cl}(t)} + ... \tag{18}$$

We can make evaluation of the partial derivatives more practical by two methods. One is to change the derivative variables to time t and temperature T using partial derivative identities. For example, we can replace the terms in the above equation using

$$\left(\frac{\partial G_{cl}(t)}{\partial C_{cl}(t)}\right)_{C_{cl}(0)} = \frac{1}{C'_{cl}(t)}\frac{dG_{cl}(t)}{dt} \tag{19}$$

$$\left(\frac{\partial G_{cl}(t)}{\partial C_{cl}(0)}\right)_{C_{cl}(t)} = \frac{T}{C_{cl}(0)}\left(\frac{\partial G_{cl}(t)}{\partial T}\right)_t - \frac{1}{C'_{cl}(t)}\frac{C_{cl}(t)}{C_{cl}(0)}\frac{dG_{cl}(t)}{dt} \tag{20}$$

Here, and hereafter, we omit the notation of fixed temperature $()_T$ from the time derivatives, as usual. In obtaining eq 20, we have assumed that the spectral density $J(\omega)$ is independent of temperature, namely, $\partial C_{cl}(t)/\partial T = C_{cl}(t)/T$. This restriction could be relaxed.

Defining the derivative correlation functions, $G(t)_{n,m}$, as

$$G(t)_{n,m} \equiv \langle \partial^n f\{q(t)\}/\partial q(t)^n \cdot \partial^m g\{q(0)\}/\partial q(0)^m \rangle \tag{21}$$

we can obtain alternative derivative expressions in terms of $G(t)_{n,m}$, namely

$$\left(\frac{\partial G_{cl}(t)}{\partial C_{cl}(t)}\right)_{C_{cl}(0)} = \sum_{k,l,m}\frac{C_{cl}(t)^{k-1}C_{cl}(0)^{l+m}}{(k-1)!l!m!2^{l+m}}f_{2m+k}g_{2l+k}$$

$$= \sum_{k,l,m}\frac{C_{cl}(t)^k C_{cl}(0)^{l+m}}{k!l!m!2^{l+m}}f_{2m+k+1}g_{2l+k+1} = \left\langle\frac{\partial f(t)}{\partial q(t)}\cdot\frac{\partial g(0)}{\partial q(0)}\right\rangle_{cl} = G_{cl}(t)_{1,1} \tag{22}$$

$$\left(\frac{\partial G_{cl}(t)}{\partial C_{cl}(0)}\right)_{C_{cl}(t)} = \{G_{cl}(t)_{2,0} + G_{cl}(t)_{0,2}\}/2 \tag{23}$$

Note that $G(t) = G(t)_{0,0}$ and $\partial G_{cl}(t)/\partial C_{cl}(0) = G_{cl}(t)_{2,0}$ when $f = g$.

To obtain our working equation, and consistent with the expansion in Q, we expand eq 17 in terms of $\hbar$. With the help of the relation eq 15

$$Q(t) \equiv C_{qm}(t) - C_{cl}(t) = \frac{i\beta\hbar}{2}\frac{d}{dt}C_{cl}(t) + \frac{(i\beta\hbar)^2}{12}\frac{d^2}{dt^2}C_{cl}(t) + ... \tag{24}$$

and eq 19, we can obtain the following result, correct thorough order $\hbar^2$

$$G_{qm}(t) = G_{cl}(t) + \frac{i\beta\hbar}{2}G'_{cl}(t) + \frac{(i\beta\hbar)^2}{8}G''_{cl}(t)$$

$$- \frac{(i\beta\hbar)^2}{24}\frac{C''_{cl}(t)G'_{cl}(t)}{C'_{cl}(t)} + \frac{(i\beta\hbar)^2 C''_{cl}(0)}{12}\left(\frac{\partial G_{cl}(t)}{\partial C_{cl}(0)}\right)_{C_{cl}(t)} + ... \tag{25}$$

The last term can be calculated using eqs 20 or 23. The term is zero for the case where $G_{cl}(t)$ can be represented fully as a function of $C_{cl}(t)$, such as the linear coupling case because the differentiation of $G_{cl}(t)$ is on the fixed $C_{cl}(t)$ surface. The fourth term of eq 25 has an apparent singularity at $C'_{cl}(t) = 0$. However, for the harmonic bath, the following relation holds

$$G'_{cl}(t) = C'_{cl}(t)G_{cl}(t)_{1,1}, \tag{26}$$

so that $G'_{cl}(t)$ is also zero when $C'_{cl}(t) = 0$. Although this relation does not hold for an anharmonic bath, in the spirit of the other approximations, we can substitute this result into eq 25 to obtain the singularity-free equation

$$G_{qm}(t) = G_{cl}(t) + \frac{i\beta\hbar}{2}G'_{cl}(t) + \frac{(i\beta\hbar)^2}{8}G''_{cl}(t)$$

$$- \frac{(i\beta\hbar)^2}{24}C''_{cl}(t)G_{cl}(t)_{1,1} + \frac{(i\beta\hbar)^2 C''_{cl}(0)}{12}\left(\frac{\partial G_{cl}(t)}{\partial C_{cl}(0)}\right)_{C_{cl}(t)} + ... \tag{27}$$

All terms on the right-hand side of eq 27 are obtainable from analytic equations or, more importantly, from classical molecular dynamics simulation. Hence, in principle, we can get the quantum correlation function without any quantum calculation, within the validity of the approximations made. The method is exact through order $\hbar^2$ for a harmonic bath, and the detailed balance condition $G(t)^* = G(t - i\beta\hbar)$ also holds to this order.[11] We consider this last point further below. In principle, this result will start to deviate from exact results when the anharmonicity of the bath increases and/or quantum effects increase. The anharmonic error may be corrected by considering anharmonicity in the above derivation, for example by corrections to eqs 12 and 24. The latter truncation error may be corrected by expanding to higher order in $\hbar$. However, both corrections will make the relation more complex.

In particular, we can expand eq 17 up to $\hbar^3$ order in the same manner to obtain

$$G_{qm}(t) = G_{cl}(t) + i\beta\hbar\frac{G'_{cl}(t)}{2} + (i\beta\hbar)^2\left\{\frac{G''_{cl}(t)}{8} - \frac{C''_{cl}(t)}{C'_{cl}(t)}\frac{G'_{cl}(t)}{24} + \frac{C''_{cl}(0)}{12}\frac{\partial G_{cl}(t)}{\partial C_{cl}(0)}\right\} + (i\beta\hbar)^3\left\{\frac{G'''_{cl}(t)}{48} - \frac{C''_{cl}(t)}{C'_{cl}(t)}\frac{G''_{cl}(t)}{48} - \frac{C'''_{cl}(t)}{C'_{cl}(t)}\frac{G'_{cl}(t)}{48} + \frac{C''_{cl}(t)^2}{C'_{cl}(t)^2}\frac{G'_{cl}(t)}{48} + \frac{C''_{cl}(0)}{24}\frac{\partial G'_{cl}(t)}{\partial C_{cl}(0)}\right\} \quad (28)$$

To evaluate higher order $\hbar$ terms requires the value of higher order derivatives, which may present numerical challenges, but we anticipate that one can rely on various interpolation methods to reduce statistical noise.[18]

These expressions provide estimates of quantum CFs only from the classically calculable values. In particular, the quantum rate of vibrational energy relaxation via eq 1 is accessible, although the relations above are applicable to general CFs that can be expressed only through functions of bath coordinates q. Before testing the results, we consider some analysis below.

B. Comparison with other Approaches. Using these results, we have a useful window on the exact result that we can use to analyze other previous approximations. Expanding the known approaches in terms of $\hbar$ in the time domain, we obtain the following

$$G_{\text{standard}}(t) = G_{cl}(t) + \frac{i\beta\hbar}{2}G'_{cl}(t) - \frac{(i\beta\hbar)^3}{24}G'''_{cl}(t) + \ldots \quad (29)$$

$$G_{\text{harmonic}}(t) = G_{cl}(t) + \frac{i\beta\hbar}{2}G'_{cl}(t) + \frac{(i\beta\hbar)^2}{12}G''_{cl}(t) + \ldots \quad (30)$$

$$G_{\text{Schofield}}(t) = G_{cl}\left(t + \frac{i\beta\hbar}{2}\right) = G_{cl}(t) + \frac{i\beta\hbar}{2}G'_{cl}(t) + \frac{(i\beta\hbar)^2}{8}G''_{cl}(t) + \ldots \quad (31)$$

$$G_{\text{Egelstaff}}(t) = G_{cl}(\sqrt{t(t + i\beta\hbar)}) = G_{cl}(t) + \frac{i\beta\hbar}{2}G'_{cl}(t) + \frac{(i\beta\hbar)^2}{8}G''_{cl}(t) - \frac{(i\beta\hbar)^2}{8}\frac{1}{t}G'_{cl}(t) + \ldots \quad (32)$$

Comparing our result eq 25, one sees that all approaches reduce to the classical result for $\hbar = 0$ and also predict the correct first order term. This means that all approaches are valid for small quantum effect. As the quantum effect increases, all of the above approaches necessarily become erroneous (for a harmonic bath) because they fail to predict higher order terms correctly. Among them, we can expect that the Schofield and Egelstaff approaches may be better than others in that their third term in each equation above is correct, although none of the expressions above are fully correct through second order. Hence, one might expect that the accuracy depends on the model and its parameters. Indeed, Egorov et al.[11] found that the Egelstaff scheme performs better than others despite inconsistencies among model problems. These comparisons also help us to understand the variation in accuracy with system of the other approaches, evident in the figures of ref 11.

Another notable approximation is the so-called harmonic/Schofield approximation introduced by Skinner and co-workers.[11,12,19] They suggest this scheme by averaging the harmonic and Schofield schemes, which underestimate and overestimate, respectively, the vibrational relaxation rate for an exponential coupling model. For their chosen parameters, this approximation shows surprisingly accurate results. In the time domain, this alternative approximation can be expanded through order $\hbar^2$ as

$$G_{\text{harmonic/Schofield}}(t) = G_{cl}(t) + \frac{i\beta\hbar}{2}G'_{cl}(t) + \frac{5(i\beta\hbar)^2}{48}G''_{cl}(t) + \ldots \quad (33)$$

By comparison to eq 31, one sees that the third term here is smaller than that in the Schofield scheme. One can see how this then compensates for overestimation in this model. However, this scheme is not analytically more justified than others, and therefore may be expected to also lack consistency when applied to different model systems.

For future reference, the above schemes are represented in the frequency space by

$$\tilde{G}_{\text{standard}}(\omega) = \frac{2}{1 + \exp(-\beta\hbar\omega)}\tilde{G}_{cl}(\omega) \quad (34)$$

$$\tilde{G}_{\text{harmonic}}(\omega) = \frac{\beta\hbar\omega}{1 - \exp(-\beta\hbar\omega)}\tilde{G}_{cl}(\omega) \quad (35)$$

$$\tilde{G}_{\text{Schofield}}(\omega) = \exp(\beta\hbar\omega/2)\tilde{G}_{cl}(\omega) \quad (36)$$

$$\tilde{G}_{\text{Egelstaff}}(\omega) = \exp(\beta\hbar\omega/2)\int_{-\infty}^{\infty} dt\, \exp(i\omega t) G_{cl}\{\sqrt{t^2 + (\beta\hbar/2)^2}\} \quad (37)$$

$$\tilde{G}_{\text{harmonic/Schofield}}(\omega) = \exp(\beta\hbar\omega/4)\sqrt{\frac{\beta\hbar\omega}{1 - \exp(-\beta\hbar\omega)}}\tilde{G}_{cl}(\omega) \quad (38)$$

With the aid of the correct $\hbar^2$ order expansion in eq 25, we can improve the widely used Schofield and Egelstaff schemes to reproduce the correct $\hbar^2$ terms, if one neglects the terms involving $\partial G_{cl}(t)/\partial C_{cl}(0)$. We then find the following *extended* Egelstaff and Schofield schemes

$$G_{\text{E\_Egelstaff}}(t) = G_{cl}\left(\sqrt{t^2 + i\beta\hbar t + (i\beta\hbar)^2\left(\frac{1}{4} - \frac{t}{12}\frac{C''_{cl}(t)}{C'_{cl}(t)}\right)}\right) \quad (39)$$

$$G_{\text{E\_Schofield}}(t) = G_{cl}\left(t + \frac{i\beta\hbar}{2}\right) - \frac{(i\beta\hbar)^2}{24}C''_{cl}\left(t + \frac{i\beta\hbar}{2}\right)G'_{cl}\left(t + \frac{i\beta\hbar}{2}\right)/C'_{cl}\left(t + \frac{i\beta\hbar}{2}\right) \quad (40)$$

The first, the extended Egelstaff approximation, reduces to the original Schofield scheme for the special case that $tC''_{cl}(t) = 0$ and reduces to Egelstaff when $C''_{cl}(t)/C'_{cl}(t) = 3/t$. However, it is singular when $C'_{cl}(t) = 0$. On the other hand, the latter, extended Schofield, approximation actually reproduces the terms through $\hbar^3$ order correctly (see eq 28) except those that include $\partial G_{cl}(t)/\partial C_{cl}(0)$ derivatives. Further, we can use the relation of eq 26 to avoid singularity. With that substitution, eq 40 becomes

$$G_{\mathrm{E\_Schofield}}(t) = G_{cl}\left(t + \frac{i\beta\hbar}{2}\right) - \frac{(i\beta\hbar)^2}{24} C''_{cl}\left(t + \frac{i\beta\hbar}{2}\right) G_{cl}\left(t + \frac{i\beta\hbar}{2}\right)_{1,1} \quad (41)$$

We test the usefulness of this result in the next section.

III. Numerical Results

In this section, we implement the primary results of this paper for two specific models for which both the exact result and that of all other approximations discussed can be evaluated. These two exactly solvable models are linear coupling $G(t) = \langle q(t)q(0)\rangle$ and exponential coupling $G(t) = \langle e^{q(t)}e^{q(0)}\rangle - \langle e^{q(0)}\rangle^2$. The last model is only apparently different from the definition of CF eq 4; it can be put in that form by incorporating a displacement by the mean value in the definition of the correlated function. The linear coupling case is of interest because it allows us to readily test the impact of the truncated series representations characterizing our present results.

For explicit calculations, we specify the form of the spectral density as in earlier work[11]

$$J(\omega) = 2\lambda\omega^{\alpha}/\omega_0^{\alpha+1} e^{-\omega^2/\omega_0^2} \quad (42)$$

with $\alpha = 1$ (Ohmic) or $\alpha = 3$ (super-Ohmic). Note that $J(\omega)$ is normalized as $\int_0^\infty d\omega J(\omega) = \lambda$. Fortunately, analytical expressions for $C_{cl}(t)$ are available for these spectral densities, namely

$$C_{cl}(t) = \frac{2\lambda\sqrt{\pi}}{\beta\omega_0} \exp\left(-\frac{1}{4}\omega_0^2 t^2\right) \quad (\alpha = 1) \quad (43)$$

$$C_{cl}(t) = \frac{\lambda\sqrt{\pi}}{2\beta\omega_0}(2 - \omega_0^2 t^2) \exp\left(-\frac{1}{4}\omega_0^2 t^2\right) \quad (\alpha = 3) \quad (44)$$

From these functions, the analytical expressions of Schofield and Egelstaff approaches can be obtained by the first equality in eqs 31 and 32, respectively. And we can Fourier transform these functions analytically

$$\tilde{C}_{cl}(\omega) = \frac{4\lambda\pi}{\beta\omega_0^2} \exp\left(-\frac{\omega^2}{\omega_0^2}\right) \quad (\alpha = 1) \quad (45)$$

$$\tilde{C}_{cl}(\omega) = \frac{4\lambda\pi\omega^2}{\beta\omega_0^4} \exp\left(-\frac{\omega^2}{\omega_0^2}\right) \quad (\alpha = 3) \quad (46)$$

The expressions of $\tilde{C}_{qm}(\omega)$ can be obtained from these functions and eq 10. We set $\lambda = 0.2$, $\omega_0 = 1.0$, and $\hbar = 1.0$ in all calculations below.

A. Linear Coupling. For the linear coupling case, the relation $G(t) = C(t)$ simplifies eq 25 to

$$C_{qm}(t) \sim C_{cl}(t) + \frac{i\beta\hbar}{2} C'_{cl}(t) + \frac{(i\beta\hbar)^2}{12} C''_{cl}(t) \quad (47)$$

These are the first three terms in the expansion of the harmonic approximation eq 30. We note that the (infinite order) "harmonic" approximation scheme is exact for linear coupling.

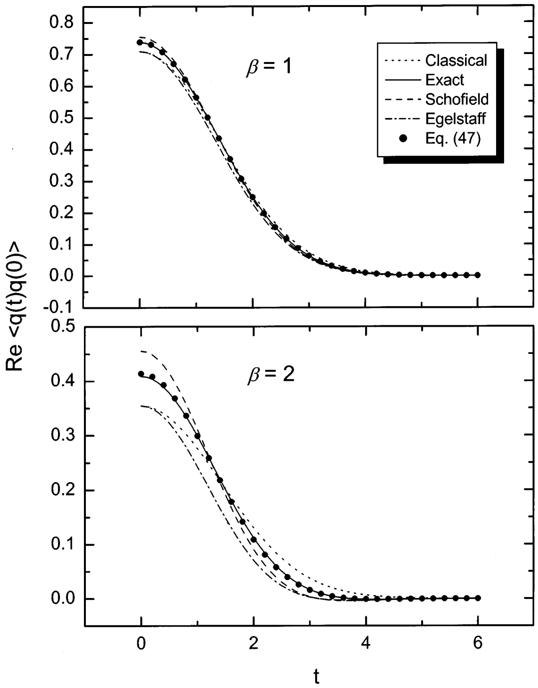

Figure 1. Time dependence of the real part of $\langle q(t)q(0)\rangle$ for $\beta = 1$ and 2. The Ohmic spectral density is used. The classical result is obtained from eq 43. The Schofield and Egelstaff results are obtained from the first equality in relations eqs 31 and 32 and the classical result, respectively. The exact result is from inverse Fourier transform of eq 10 with eq 45.

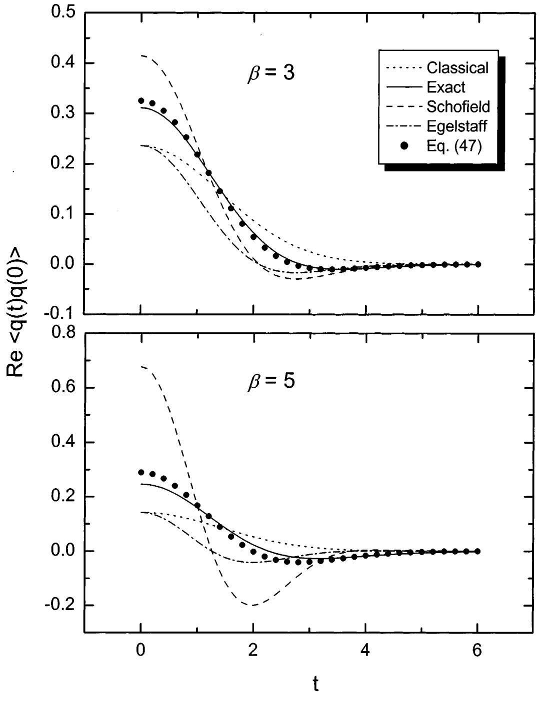

Figure 2. Time dependence of the real part of $\langle q(t)q(0)\rangle$ for $\beta = 3$ and 5. The Ohmic spectral density is used. The results are obtained by the same method as in Figure 1.

In Figures 1 and 2, we compare our series results eq 47 for the real part of the CF with others, for various temperatures, using the Ohmic spectral density ($\alpha = 1$). For $\beta = 1.0$ when the quantum effect is not large, all approaches show excellent agreement with the exact result. As the temperature is lowered, the predictions of approximations start to deviate from the exact result. Although the classical result relaxes more slowly, the

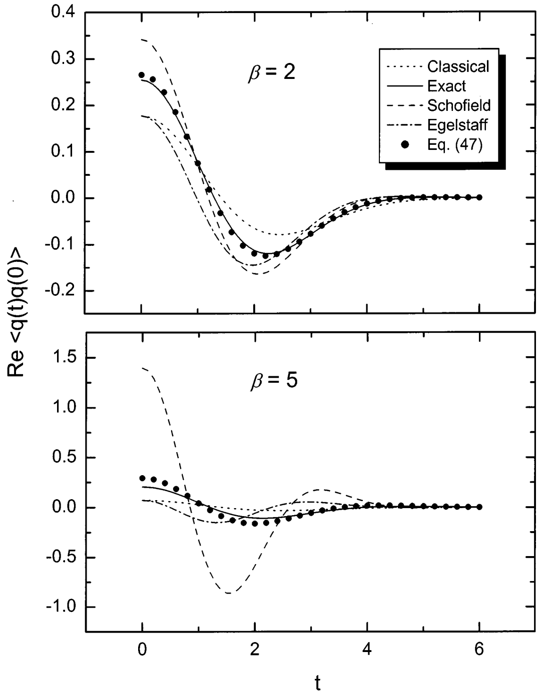

Figure 3. Time dependence of the real part of $\langle q(t)q(0)\rangle$ for $\beta = 2$ and 5. The super-Ohmic spectral density is used. The results are obtained by the same method as in Figure 1 except that the classical results are given by eqs 44 and 46.

results of Schofield and Egelstaff approximation show faster relaxation than the exact result. For $\beta = 5.0$, the Schofield approach shows very poor prediction. Note that this effect will diverge with β, since $C_{\text{Schofield}}(t) = C_{cl}(t)e^{(\beta\hbar\omega)^2/16}e^{i\beta\hbar t}$. The new result, based on the truncated series in eq 47, is evidently superior to all other approximations shown for all temperatures. Although the results are nearly indistinguishable from the exact result at $\beta = 3.0$, there is some deviation for $\beta = 5.0$. However, even for that low temperature, our result still follows the exact result strikingly, and perhaps surprisingly well, considering that it is based on a low order series. In Figure 3, we plot the same CFs for $\alpha = 3$, and they show the same trend as Figures 1 and 2.

For results in Fourier transformed space, eq 47 can be represented by

$$\tilde{C}_{qm}(\omega) \sim \left\{1 + \frac{\beta\hbar\omega}{2} + \frac{(\beta\hbar\omega)^2}{12}\right\}\tilde{C}_{cl}(\omega) \qquad (48)$$

Fourier transformed CF is plotted in Figure 4 for various approximations, using the super-Ohmic spectral density. Overall accuracy improves because the imaginary term (first order in $\hbar$) contributes in the Fourier transformed domain. With the exception of the Egelstaff approximation, all approaches predict correctly that $\tilde{C}_{qm}(0) = \tilde{C}_{cl}(0)$. The close agreement of the current method with the exact result is again surprising. Even for the very low temperature $\beta = 10.0$, the present method is nearly indistinguishable from the exact result, while the Schofield and Egelstaff approximations predict nearly meaningless results. The classical result is more accurate than these two infinite order approximations. The figure demonstrates that in this case, neglecting higher order terms is a better approximation than keeping incorrect terms, particularly for large quantum effects.

One might have expected the extended Schofield approximation eq 40 to be the best of all schemes considered here because it correctly reproduces the lower order $\hbar$ order terms, but is an infinite order approximation. However, as evident in the Figure 5, it is clear that, in contrast to the truncated series result, this extended approximation manifests large errors for the case of large $\beta\hbar$, where the higher order terms are more important. We believe that this fact can be attributed to the structure of higher order terms. Although the magnitude of individual higher order

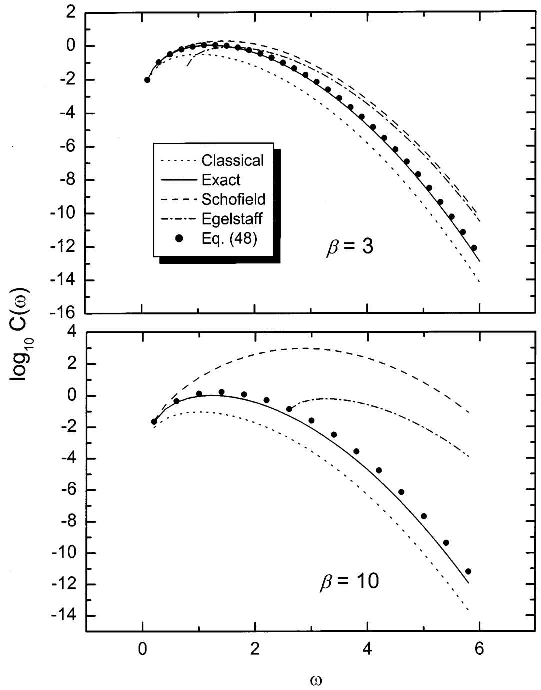

Figure 4. Frequency dependence of the Fourier transformed $\langle q(t)q(0)\rangle$ for $\beta = 3$ and 10. The super-Ohmic spectral density is used. The classical result is obtained from eqs 46. The exact, Schofield, and Egelstaff results are obtained form the relations eqs 10, 36, and 37 along with the classical result, respectively.

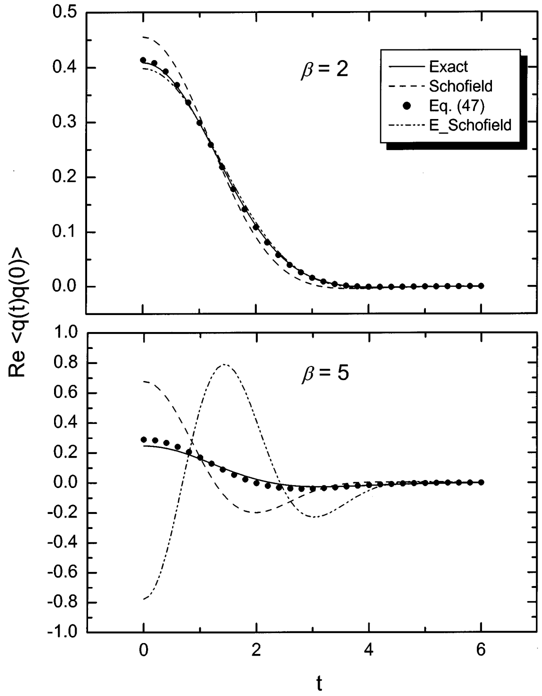

Figure 5. Time dependence of the real part of $\langle q(t)q(0)\rangle$ for $\beta = 2$ and 5. The Ohmic spectral density is used. The results are obtained by the same method as in Figure 1. The result of the extended Schofield approximation eq 41 is also shown for comparison.

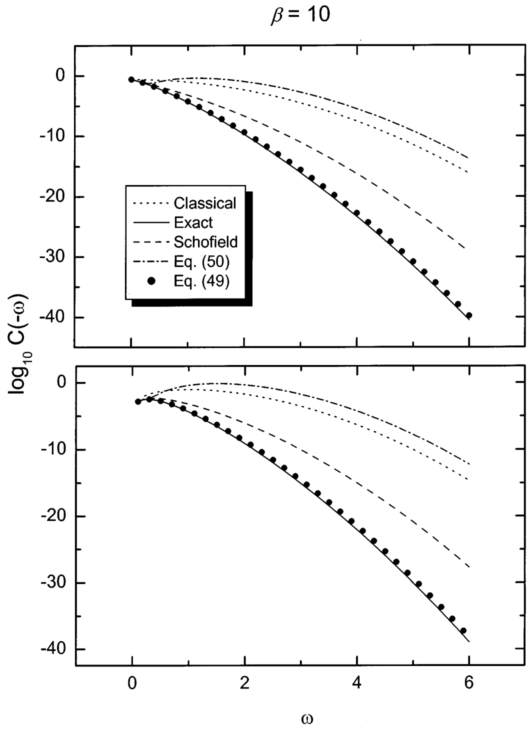

Figure 6. Frequency dependence of $\tilde{C}(-\omega)$ for $\beta = 10$. The Ohmic (upper panel) and super-Ohmic (lower panel) spectral density are used. The results are obtained from eq 49, with $\tilde{C}(\omega)$ determined by the same method as in Figure 4, except that the classical result is given by eq 45 in the lower panel.

terms increase with the value of $\beta\hbar$, the sum of higher order terms is evidently not large and their values must somehow effectively cancel each other. By expanding eq 9 or eq 10 to higher order, one can confirm that the sign of these terms appears to alternate. Consequently, we find strong evidence that ignoring higher order terms is preferred to the incorrect infinite order summation, at least for the models considered here.

As previously mentioned, the truncated solution satisfies the detailed balance condition in the frequency space

$$\tilde{G}_{qm}(-\omega) = e^{-\beta\hbar\omega}\tilde{G}_{qm}(\omega) \tag{49}$$

only to the truncated order. In other words, for $\hbar^2$ order, eq 49 becomes

$$\tilde{G}_{qm}(-\omega) \sim \left\{1 - \beta\hbar\omega + \frac{(\beta\hbar\omega)^2}{2}\right\}\tilde{G}_{qm}(\omega) \tag{50}$$

However, when the value of $\beta\hbar\omega$ is much larger than unity, eq 50 is expected to fail numerically because the exponential function in eq 49 is not well described by the polynomial factor in eq 50. Thus, the value of Fourier transformed CF for the negative frequency $\tilde{G}(-\omega)$ obtained from the truncated solution eq 25 will likely be erroneous. This can be understood since for negative frequency, the effective cancellation of the values of higher $\hbar$ order terms does not work since the signs of the terms change. We can overcome this limitation readily by using eq 49 instead of eq 50 for negative frequency. To test this, we plot $\tilde{C}(-\omega)$ for $\beta = 10.0$ for both spectral densities in Figure 6. The results from eq 50 are worse than even the classical results, where $\tilde{G}_{cl}(-\omega) = \tilde{G}_{cl}(\omega)$. However, the present method using eq 49 gives very accurate results up to order 10^{-40} for negative frequency. Therefore, we conclude that eq 25 should be used for positive frequency and eq 49 with eq 25 should be used for negative frequency.

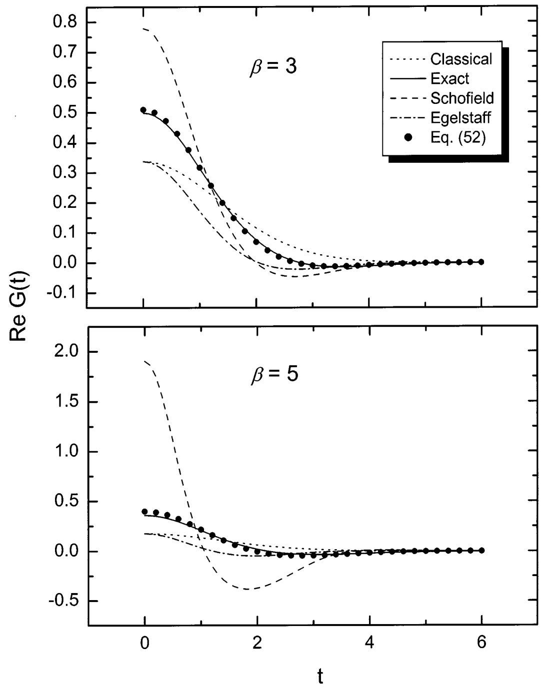

Figure 7. Time dependence of the real part of $\langle \exp\{q(t)\}\exp\{q(0)\}\rangle - \langle \exp\{q(0)\}\rangle^2$ for $\beta = 3$ and 5. The Ohmic spectral density is used. The exact results are obtained from eq 51, and the analytical result for $C(t)$.

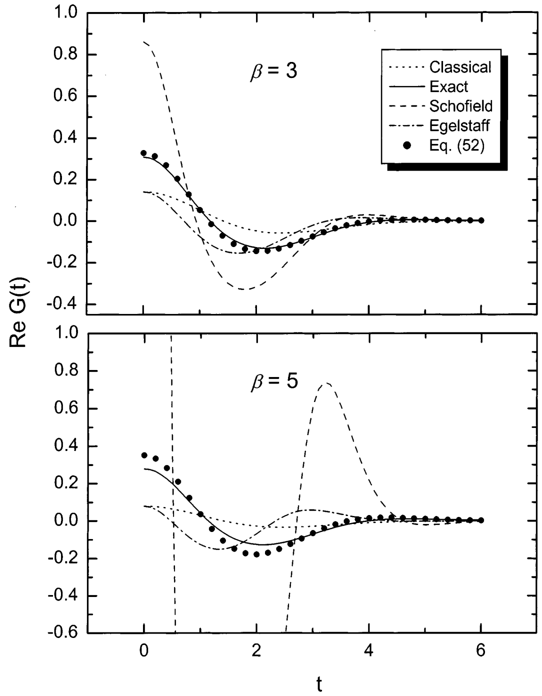

Figure 8. Time dependence of the real part of $\langle \exp\{q(t)\}\exp\{q(0)\}\rangle - \langle \exp\{q(0)\}\rangle^2$ for $\beta = 3$ and 5. The super-Ohmic spectral density is used. The results are obtained by the same method as in Figure 7.

B. Exponential Coupling. For the exponential coupling $F = \exp(q)$

$$G(t) = \exp\{C(0)\}[\exp\{C(t)\} - 1] \tag{51}$$

holds, and our result for this coupling is given by eq 25

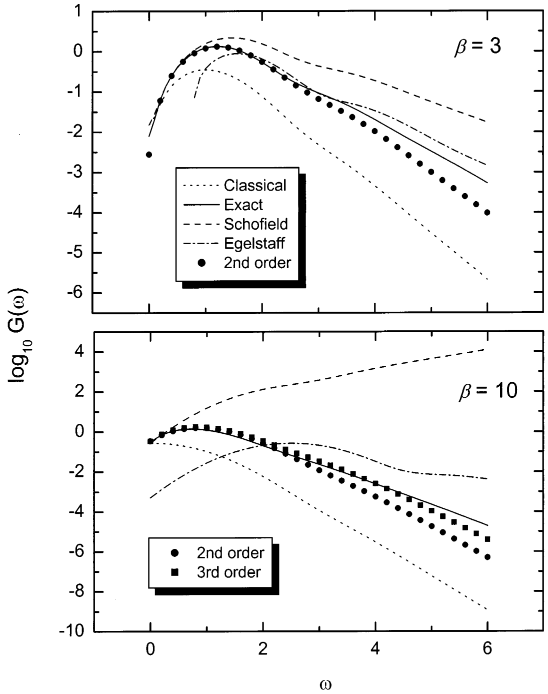

Figure 9. Frequency dependence of the Fourier transformed $\langle \exp\{q(t)\}\exp\{q(0)\}\rangle - \langle \exp\{q(0)\}\rangle^2$ for $\beta = 3$ and 10. The Ohmic spectral density is used. The exact results are obtained by the Fourier transform of eq 51. The second and third order curves are obtained by the Fourier transform of eq 52 and eq 28, respectively.

$$G_{qm}(t) \sim G_{cl}(t) + \frac{i\beta\hbar}{2}G'_{cl}(t) + \frac{(i\beta\hbar)^2}{8}G''_{cl}(t) - \frac{(i\beta\hbar)^2}{24}C''_{cl}(t)\exp\{C_{cl}(0) + C_{cl}(t)\} + \frac{(i\beta\hbar)^2 C''_{cl}(0)G_{cl}(t)}{12} \quad (52)$$

Note that in this case, $\partial G(t)/\partial C(0) = G(t)$. In Figures 7 and 8, we plot $G(t)$ for $\alpha = 1$ and 3, respectively. For the indicated temperatures, the accuracy of the present approximation is evidently better than that for the linear coupling case discussed above. In Figure 9, we plot $\tilde{G}(\omega)$ on a log scale. For this case, the Fourier transform of $G(t)$ is obtained numerically. The superior performance of the present approach is again evident, although some errors do appear at high frequency. Because the error results from neglecting higher order terms, we consider also the extended expansion given in eq 28 through $\hbar^3$. Indeed, the result is closer to the exact result. We note that the harmonic/Schofield scheme, which predicts very accurate result for high temperature,[11] is no longer accurate at low temperature, where the Schofield scheme shows very poor accuracy, as evident in Figure 9

IV. Concluding Remarks

We have presented a promising approach to obtain a quantum correlation function of bath variables from its classical result. The expression is based on use of a harmonic bath result to obtain expressions for the quantum corrections and an expansion of the correction in terms of the correction to the linear position correlation function as the small parameter. The accuracy can be further improved by expanding to higher order. The expansion has been useful in identifying the origins of the inconsistent performance of alternative approximations in earlier work, which differ from the exact result in second order in $\hbar$. The new expressions have the advantage that they require no functional form for the classical correlation functions to obtain accurate results, so that the quantum result can, in principle, be evaluated directly from simulated classical correlation functions. We also note that the expressions developed do not require the prescription of an underlying harmonic model for implementation.

We have applied the current method to two exactly solvable models involving harmonic baths and shown that its accuracy is consistently superior to other known approaches for these models. Surprisingly, when the quantum effect is larger, the difference in the accuracy between previous and present approaches is even larger, with the present approach remaining quite close to the correct result. We have attributed this fact to the tendency of higher order terms in $\hbar$ to cancel, and the errors in infinite order approximations to the failure to correctly capture this cancellation for positive frequency. This origin is indicated also by the failure at low temperature of the extended Schofield approximation, introduced in the present work. Because our derivation is based on the harmonic bath assumption, anharmonic systems will be a more severe test of the new expressions. The fact that the anharmonicity is fully treated at the classical level in the present approach provides some reason for optimizm. Results for anharmonic systems will be reported elsewhere, but preliminary results are encouraging.

Acknowledgment. The authors gratefully acknowledge the support of this research by a grant from the National Science Foundation. Additional support was provided by a grant from the R. A. Welch Foundation. H. K. is partially supported by the postdoctoral fellowship program of Korea Science and Engineering Foundation (KOSEF).

References and Notes

(1) Bader, J. S.; Berne, B. J. *J. Chem. Phys.* **1994**, *100*, 8359−8366.
(2) Egorov, S. A.; Berne, B. J. *J. Chem. Phys.* **1997**, *107*, 6050−6061.
(3) Oxtoby, D. W. *Adv. Chem. Phys* **1981**, *47*, 487−519.
(4) Heilweil, E. J.; Casassa, M. P.; Cavanagh, R. R.; Stephenson, J. C. *Annu. Rev. Phys. Chem.* **1989**, *40*, 143−171.
(5) Okazaki, S. *Adv. Chem. Phys.* **2001**, *118*, 191−270.
(6) Elsaesser, T.; Kaiser, W. *Annu. Rev. Phys. Chem.* **1991**, *42*, 83−107.
(7) Owrutsky, J. C.; Raftery, D.; Hochstrasser, R. M. *Annu. Rev. Phys. Chem.* **1994**, *45*, 519−555.
(8) Taiji Mikami; Motoyuki Shiga; Okazaki, S. *J. Chem. Phys.* **2001**, *115*, 9797−9807.
(9) Skinner, J. L. *J. Chem. Phys.* **1997**, *107*, 8717−8718.
(10) Frommhold, L. *Collision-Induced Absorption in Gases*, 1st ed.; Cambridge University Press: London, 1993; Vol. 2.
(11) Egorov, S. A.; Everitt, K. F.; Skinner, J. L. *J. Phys. Chem. A* **1999**, *103*, 9494−9499.
(12) Skinner, J. L.; Park, K. *J. Phys. Chem. B* **2001**, *105*, 6716−6721.
(13) Berne, B. J.; Harp, G. D. *Adv. Chem. Phys.* **1970**, *17*, 63.
(14) Berens, P. H.; White, S. R.; Wilson, K. R. *J. Chem. Phys.* **1981**, *75*, 515.
(15) Schofield, P. *Phys. Rev. Lett.* **1960**, *4*, 239.
(16) Egelstaff, P. A. *Adv. Phys.* **1962**, *11*, 203.
(17) Egorov, S. A.; Skinner, J. L. *J. Chem. Phys.* **1996**, *105*, 10 153−10 155.
(18) Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. *Numerical Recipes in C*; Cambridge University Press: Cambridge, 1988.
(19) Everitt, K. F.; Skinner, J. L.; Ladanyi, B. M. *J. Chem. Phys.* **2002**, *116*, 179−183.