

# A Short-Time Quantum Mechanical Expansion Approach to Vibrational Relaxation<sup>†</sup>

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The vibrational relaxation rate of a “quantum” molecule embedded in a “quantum” host is approached from the perspective of a short-time expansion of the quantum force–force time correlation function. A general path integral Monte Carlo scheme is developed to compute the coefficients of the expansion, which involve the quantum thermal average of operators that depend on *both* position and momentum. A simple ansatz is used to connect the short-time and long-time behavior of the force–force correlation function. The method is tested on a simple model problem. Improvements of the approach and further applications are discussed.

## I. Introduction

The study of the vibrational relaxation of a probe molecule in a condensed phase host has occupied a central place in physical chemistry for many years.<sup>1–4</sup> The temperature and density dependence of the vibrational relaxation rate can yield crucial information concerning the microscopic motion in the vicinity of the probe molecule, as well as the nature of the coupling of the probe to the surrounding host. A major obstacle in the theoretical modeling of vibrational relaxation is the fact that the rate is intrinsically quantum mechanical in nature.<sup>5–8</sup> Efforts to model various aspects of vibrational relaxation phenomena by treating the environment as a classical entity may lead to rates that disagree with experimental values by orders of magnitude.<sup>5,6</sup> In fact, the vigorous recent discussion in the literature concerning the accuracy of a variety of mixed quantum-classical treatments of vibrational relaxation stands as a testament to the difficulty of properly treating the quantum nature of vibrational relaxation in condensed phases.

The vibrational relaxation rate may be related to the Fourier transform of the time correlation function of the force exerted by the host on the probe molecule.<sup>1</sup> The calculation of this “force–force” correlation function should be performed quantum mechanically to ensure an accurate estimation of the relaxation rate.<sup>5,7</sup> Outside of a few isolated examples, the quantum mechanical calculation of this correlation function is not possible with current theoretical techniques. Intuitively, one expects that the high-frequency portion of the Fourier transform of the force–force correlation function is sensitive only to short-time behavior.<sup>6</sup> This type of reasoning has led to a variety of simple ansatz that use short-time information to link the short- and long-time regimes of a given correlation function.<sup>6,9,10</sup> For the vibrational relaxation problem, this approach has proved to be quite useful. In some cases, simple approaches requiring only a few coefficients of the short-time Taylor expansion of the force–force correlation function have yielded nearly quantitative

results for the *classical* bath approximation to the vibrational relaxation rate for oscillators with intrinsic vibrational frequencies greater than about 150 cm<sup>−1</sup>.<sup>6</sup>

One should note that techniques that rely on short-time expansions are ubiquitous in statistical mechanics. For example, in standard kinetic and mode-coupling theories of liquids, the “binary” portion of the memory function for a given time correlation function is calculated through the knowledge of the short-time Taylor coefficients of the memory function under study.<sup>11</sup> The “viscoelastic” theory of collective density fluctuations in liquids involves a continued fractional representation of the memory function.<sup>11</sup> The input to this continued fractional approach is obtained from a short-time expansion of the longitudinal current correlation function.

In this paper, we shall investigate the possibility of calculating the *quantum mechanical* vibrational relaxation rate from a quantum Taylor expansion of the force–force correlation function. This procedure involves the computation of the coefficients of the Taylor expansion of the *quantum* force–force correlation function. While these coefficients may be calculated via techniques of *equilibrium* quantum statistical mechanics, the calculation of such terms is nontrivial. This is because the simulation of quantum static averages that involve both momentum *and* position is a difficult task, in general. In fact, we could find in the literature no general attempt to calculate such averages for realistic systems. Here, we show that such averages may indeed be computed in realistic systems. While we focus here on a primitive means to use this information to obtain vibrational relaxation rates, more sophisticated approaches may be used that also rely on the same short-time information.<sup>12</sup> Furthermore, the same techniques may be used to compute other quantities, as alluded to in the last paragraph. A discussion of these additional uses of the methods developed in this work will be given in the final section of this paper.

Bruce Berne has been a pioneer in theoretical chemistry for over thirty years. Some of his favorite topics, including quantum Monte Carlo, the analysis of mixed quantum-classical methods, and, of course, vibrational relaxation in condensed media, are

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touched upon in this work. It is a great honor for us to dedicate this work to him on the occasion of his sixtieth birthday.

## II. Model Hamiltonian and Vibrational Energy Relaxation Rate

In this section we define the model Hamiltonian used to study the vibrational energy relaxation rate and provide a brief formulation of the rate in terms of a time-dependent correlation function. A detailed discussion of the vibrational energy relaxation rate for this model has recently been given by Egorov and Berne,<sup>7</sup> and also reviewed by Egorov et al.<sup>13</sup>

We consider the relaxation of a vibrationally excited molecule embedded in a condensed phase environment. We assume (without loss of generality) that the Hamiltonian can be written as follows:

$$H = H_s + H_b + V = H_0 + V \quad (1)$$

where  $H_s$  is the harmonic Hamiltonian of the solute vibrational displacement  $q$ , with a conjugate momentum  $p$ , frequency  $\omega_0$ , and a reduced mass  $m$ :

$$H_s = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 q^2 \quad (2)$$

We model the condensed phase environment as a harmonic bath and take  $H_b$  in eq 1 to be a sum over harmonic mass-weighted normal modes  $Q_\alpha$  with frequencies  $\omega_\alpha$  and conjugate momenta  $P_\alpha$ :

$$H_b = \frac{1}{2} \sum_{\alpha} (P_{\alpha}^2 + \omega_{\alpha}^2 Q_{\alpha}^2) \quad (3)$$

The interaction term between the solute and the solvent is taken to be linear in the solute displacement and exponential function of the bath collective coordinate  $Q = \sum_{\alpha} g_{\alpha} Q_{\alpha}$ .<sup>7</sup>

$$V = \gamma q e^Q = \gamma q F(Q) \quad (4)$$

The effect of the bath on the system is completely determined by the spectral density  $J(\omega)$ :

$$J(\omega) = \sum_{\alpha} \frac{g_{\alpha}^2}{2\omega_{\alpha}} \delta(\omega - \omega_{\alpha}) \quad (5)$$

All of the results shown in the paper were obtained for a super-Ohmic spectral density of the form

$$J(\omega) = 2\eta\omega^3/\omega_c^2 \exp(-(\omega/\omega_c)^2) \quad (6)$$

where  $\eta$  is an overall coupling strength, and  $\omega_c$  is the cutoff frequency (for numerical convenience we have replaced the sharp cutoff at the Debye frequency with a smooth Gaussian cutoff).

In what follows, we will focus on two particular states of the molecule, which we label as  $|0\rangle$  and  $|1\rangle$ . Using the lowest order golden rule perturbation theory, the transition rate from state  $|1\rangle$  to state  $|0\rangle$  is given by (from now on we employ atomic units, i.e.,  $\hbar = 1$ )

$$k_{1 \rightarrow 0} = \gamma^2 |q_{10}|^2 \int_{-\infty}^{\infty} dt \exp(i\omega_0 t) C(t) \quad (7)$$

where

$$C(t) = \langle \delta F(0) \delta F(t) \rangle = \langle F(0) F(t) \rangle - \langle F(0) \rangle^2 \quad (8)$$

In the above  $\langle \dots \rangle = \text{Tr}(\rho_0 \dots)$  denotes the trace over the system and bath coordinates, the equilibrium density operator is given by  $\rho_0 = \exp(-\beta H_0)/Z$ ,  $\beta = 1/k_B T$  is the inverse temperature,  $Z = \text{Tr} \exp(-\beta H_0)$ , and  $F$  is defined in eq 4.

The vibrational relaxation rate can be formulated in terms of the Kubo transform<sup>14</sup> of the force–force correlation function:

$$\psi(t) = \frac{1}{\beta} \int_0^{\beta} d\lambda C(t + i\lambda) \quad (9)$$

and in terms of this transform the rate reads

$$k_{1 \rightarrow 0} = K(\omega_0) \gamma^2 |q_{10}|^2 \int_{-\infty}^{\infty} dt \exp(i\omega_0 t) \psi(t) \quad (10)$$

where

$$K(\omega_0) = \frac{\beta\omega_0}{2} (\coth(\beta\omega_0/2) + 1) \quad (11)$$

The Kubo transform has been used as a starting point for many approximate methods, such as the centroid molecular dynamics method.<sup>15</sup> However, the vibrational relaxation rate given by eqs 9–11 is an *exact quantum mechanical* formalism, because at this point we have made no approximation to the quantum mechanical time propagation. We adopt the Kubo formalism because it is convenient (involving only even time moments), and among the different possibilities we find the Kubo formalism the most stable numerically (see also ref 12).

With the exponential form for the system–bath coupling, the thermal averaging in eq 8 can be performed using standard boson algebra identities.<sup>7,16</sup> The force–force time correlation function is given by

$$C(t) = \exp(\phi(t)) - \exp(\phi(0)/2) \quad (12)$$

where  $\phi(t)$  is given by

$$\phi(t) = \frac{1}{2} \sum_{\alpha} \frac{g_{\alpha}^2}{\omega_{\alpha}} \left[ (1 + \cos(\omega_{\alpha} t)) \coth\left(\frac{\beta\omega_{\alpha}}{2}\right) - i \sin(\omega_{\alpha} t) \right] \quad (13)$$

Inserting the analytic expression for  $C(t)$  into eq 7 and integrating over time yields the exact quantum mechanical relaxation rate for this model.

## III. Short-Time Expansion

The expression for the transition rate from state  $|1\rangle$  to state  $|0\rangle$  given in eq 7 is not limited to the model described in the previous section. However, the exact numerical solution of this problem for a general anharmonic bath is extremely complicated. To be more specific, the time propagation of a general form of the coupling force  $F$  is computationally impractical due to rapid phase oscillations (the numerical “sign” problem).

At the present time, one viable alternative to the exact quantum mechanical solution is the use of mixed quantum–classical treatments, in which a small subset of highly “quantum” modes is treated quantum mechanically while the remaining degrees of freedom are treated classically. For the vibrational relaxation problem, this procedure amounts to replacing the quantum  $C(t)$  by its classical approximation.<sup>1</sup> The major issues associated with this approach have been discussed by Bader and Berne<sup>17</sup> and others<sup>18</sup> for *single* phonon vibrational relaxation processes, and by Egorov and Berne<sup>7</sup> and Nitzan and collabora-

tors<sup>19</sup> for the *multiphonon* case. It was found that the mixed quantum-classical approach may lead to significant errors in the vibrational relaxation rate, and a fully classical approach is superior, yet not satisfactory.<sup>13</sup>

An attempt to improve the mixed quantum-classical approximation is to relate the classical time correlation function to the quantum counterpart by modifying the classical time correlation function in the time or frequency domain.<sup>20,21</sup> The accuracy of these “quantum correction” methods has been assessed in the context of vibrational relaxation,<sup>8,22</sup> and unfortunately the different procedures can differ widely from each other, and no single procedure is completely satisfactory.<sup>8,22</sup>

The approach we adopt here is based on a short-time expansion of the Kubo time correlation function in eq 9. The Kubo correlation function at long times is obtained from a simple analytic ansatz

$$\psi(t) = \psi(0) \frac{\cos(bt)}{\cosh(at)} \quad (14)$$

This form was suggested by Douglass<sup>10</sup> and was used previously by Skinner and co-workers<sup>6,9</sup> in the context of vibrational relaxation. The complex coefficients  $a$  and  $b$  are determined by requiring that the short-time expansion of eq 14 through fourth order in time agree with the exact correlation function, and are given by:<sup>6</sup>

$$\begin{aligned} a &= \frac{1}{2} \sqrt{\frac{\psi_4}{\psi_2} - \frac{\psi_2}{\psi_0}} \\ b &= \frac{1}{2} \sqrt{\frac{5\psi_2}{\psi_0} - \frac{\psi_4}{\psi_2}} \end{aligned} \quad (15)$$

In the above equation

$$\psi_0 = \frac{1}{\beta Z} \int_0^\beta d\lambda \text{Tr} e^{-(\beta-\lambda)H_0} F e^{-\lambda H_0} F \quad (16)$$

$$\psi_2 = \frac{1}{\beta Z} \int_0^\beta d\lambda \text{Tr} e^{-(\beta-\lambda)H_0} \dot{F} e^{-\lambda H_0} \dot{F} \quad (17)$$

$$\psi_4 = \frac{1}{\beta Z} \int_0^\beta d\lambda \text{Tr} e^{-(\beta-\lambda)H_0} \ddot{F} e^{-\lambda H_0} \ddot{F} \quad (18)$$

and  $\dot{F} = i[H, F]$  denotes the time derivative. For the Hamiltonian described in eq 1, the first and second time derivatives of the coupling force are given by

$$\dot{F} = \frac{1}{2} \sum_\alpha \left( P_\alpha \frac{\partial F}{\partial Q_\alpha} + \frac{\partial F}{\partial Q_\alpha} P_\alpha \right) \quad (19)$$

and

$$\begin{aligned} \ddot{F} = & \frac{1}{2} \sum_{\alpha, \alpha'} \left( P_\alpha P_{\alpha'} \frac{\partial^2 F}{\partial Q_\alpha \partial Q_{\alpha'}} + \frac{\partial^2 F}{\partial Q_\alpha \partial Q_{\alpha'}} P_\alpha P_{\alpha'} \right) + \\ & \frac{1}{4} \left( \sum_{\alpha, \alpha'} \frac{\partial^4 F}{\partial Q_\alpha^2 \partial Q_{\alpha'}^2} - \sum_\alpha \omega_\alpha^2 Q_\alpha \frac{\partial F}{\partial Q_\alpha} \right) \end{aligned} \quad (20)$$

respectively. The parameters  $a$  and  $b$  can be obtained from the three equilibrium averages given by eqs 16–18. The numerical method which we have developed to obtain these averages is described in the next section.

An alternative approach to obtain the Kubo correlation function at long times is based on the quantum mode-coupling theory (QMCT). Both the ansatz approach and the quantum mode-coupling theory require similar short-time information, namely similar thermal averages over the coupling force and its time derivatives. Because the goal of this paper is to develop a path integral Monte Carlo approach for these averages, we adopt the simpler ansatz approach here, reserving the discussion of the more involved QMCT for future work.<sup>12</sup>

#### IV. Path Integral Monte Carlo Scheme

The short-time expansion coefficients of the Kubo correlation function involve a thermal average over an operator that combines positions and momenta operators as given by eqs 19 and 20. The calculational rules for momentum-dependent operators can be tricky.<sup>23</sup> Two methods have been proposed in the literature to calculate the expectation value of the kinetic energy operator: the “direct” approach introduced by Barker,<sup>24</sup> and the virial estimator introduced by Herman, Bruskin, and Berne.<sup>25</sup> Cao and Berne have shown that the virial estimator is far more accurate compared to the direct approach for the kinetic energy operator; however, the results depend on the Monte Carlo algorithm used.<sup>26</sup>

Because a virial based approach requires higher spatial derivatives of the coupling force  $F$ , which for a more general form than that considered here are extremely tedious to obtain, we have developed a “direct” approach that is closely related to the Barker kinetic energy estimator. Because the direct approach is less accurate compared to the virial estimator, we have introduced some modifications that improve the estimate of the thermal average over the differential operator. The results shown in section V provide evidence for the robustness of the method and its accuracy. We note in passing that the finite difference method introduced recently by Rabani et al.<sup>27</sup> for the study of barrier crossing in solutions is not appropriate when the thermal average involves momenta operators of all bath modes, which is the case for vibrational energy relaxation.

For the sake of simplicity and clarity we provide only a derivation for the Kubo transform  $\psi_2$  given in eq 17. The derivation of  $\psi_4$  can be obtained following similar lines. The Kubo transform of  $\psi_0$  given in eq 16 does not involve momenta operators and thus can be obtained using standard path integral Monte Carlo (PIMC) techniques. Because  $H_0$  is separable in the system and bath Hamiltonians and the coupling force depends neither on the system coordinate  $q$  nor on its conjugate momentum  $p$ , the trace over the system coordinate in eq 17 can be performed analytically and leads to

$$\psi_2 = \frac{1}{4\beta} \sum_{\alpha, \alpha'} \int_0^\beta d\lambda \psi_2^{\alpha, \alpha'}(\lambda) \quad (21)$$

where

$$\begin{aligned} \psi_2^{\alpha, \alpha'}(\lambda) = & \frac{1}{Z_b} \int dQ dQ' \langle Q | e^{-(\beta-\lambda)H_b} (P_\alpha G_\alpha + G_\alpha P_\alpha) e^{-\lambda H_b} | Q' \rangle \\ & \langle Q' | (P_{\alpha'} G_{\alpha'} + G_{\alpha'} P_{\alpha'}) | Q \rangle \end{aligned} \quad (22)$$

In the above equation,  $G_\alpha = \partial F / \partial Q_\alpha$  and  $Z_b = \text{Tr} \exp(-\beta H_b)$ , where the trace is taken over the bath modes only. The interval  $\lambda$  can be discretized into  $P$  Trotter slices of size  $\epsilon = \beta/P$ , such that  $\lambda_j = j\epsilon$ , where  $j$  is the index of the slice. Inserting a complete set of states between the short imaginary time propagators, it is easy to show that

$$\psi_2^{\alpha,\alpha'}(\lambda_j) = \int d\mathbf{Q}_0 \cdots d\mathbf{Q}_{P+2} P_j(\mathbf{Q}_0, \cdots, \mathbf{Q}_{P+2}) \langle \mathbf{Q}_{P-j+1} | P_\alpha G_\alpha + G_\alpha P_\alpha | \mathbf{Q}_{P-j+2} \rangle \langle \mathbf{Q}_{P+2} | P_{\alpha'} G_{\alpha'} + G_{\alpha'} P_{\alpha'} | \mathbf{Q}_0 \rangle \quad (23)$$

where  $P_j(\mathbf{Q}_0, \cdots, \mathbf{Q}_{P+2})$  is given by

$$P_j(\mathbf{Q}_0, \cdots, \mathbf{Q}_{P+2}) = \frac{1}{Z_b} \prod_{k \neq P-j+1}^{P+1} \langle \mathbf{Q}_k | e^{-\epsilon H} | \mathbf{Q}_{k+1} \rangle \quad (24)$$

Using the coordinate representation of the matrix element of the operator  $P_\alpha G_\alpha + G_\alpha P_\alpha$  in eq 23

$$\langle \mathbf{Q}' | P_\alpha G_\alpha + G_\alpha P_\alpha | \mathbf{Q} \rangle = i \left( G_\alpha(\mathbf{Q}) \frac{\partial}{\partial Q'_\alpha} \delta(\mathbf{Q} - \mathbf{Q}') - G_\alpha(\mathbf{Q}') \frac{\partial}{\partial Q_\alpha} \delta(\mathbf{Q} - \mathbf{Q}') \right) \quad (25)$$

and the well-known relation for the Dirac delta function  $\delta(\mathbf{Q})$

$$\int d\mathbf{Q} \frac{\partial \delta(\mathbf{Q})}{\partial Q_\alpha} f(\mathbf{Q}) = - \int d\mathbf{Q} \frac{\partial f(\mathbf{Q})}{\partial Q_\alpha} \delta(\mathbf{Q}) \quad (26)$$

it is simple to show that for  $j = 1 \cdots P$

$$\begin{aligned} \psi_2^{\alpha,\alpha'}(\lambda_j) = & - \int d\mathbf{Q}_0 \cdots d\mathbf{Q}_{P+2} \delta(\mathbf{Q}_0 - \mathbf{Q}_{P+2}) \delta(\mathbf{Q}_{P-j+2} - \mathbf{Q}_{P-j+1}) \\ & \left( G_\alpha(\mathbf{Q}_{P-j+2}) \frac{\partial}{\partial Q_{\alpha'}^{P-j+1}} - G_\alpha(\mathbf{Q}_{P-j+1}) \frac{\partial}{\partial Q_\alpha^{P-j+2}} \right) \\ & \left( G_{\alpha'}(\mathbf{Q}_0) \frac{\partial}{\partial Q_{\alpha'}^{P+2}} - G_{\alpha'}(\mathbf{Q}_{P+2}) \frac{\partial}{\partial Q_{\alpha'}^0} \right) P_j(\mathbf{Q}_0, \cdots, \mathbf{Q}_{P+2}) \quad (27) \end{aligned}$$

Note that the pairs  $G_\alpha$  and  $\partial/\partial Q_\alpha$  have different arguments in eq 25. This fact is used in eq 27 to bypass the need to compute higher derivatives of the coupling force, and it turns out that it also stabilizes the Monte Carlo calculation. The “surface terms”  $j = 0$  and  $j = P + 1$  can be obtained in a similar fashion; however, their derivation is slightly more tedious because the derivative of the two delta functions (in eq 23) involves the same imaginary time-slice, and thus will not be given here. The final step in our derivation involves the differentiation of  $P_j(\mathbf{Q}_0, \cdots, \mathbf{Q}_{P+2})$  and the integration over the two delta functions in eq 27, which leads to

$$\begin{aligned} \psi_2^{\alpha,\alpha'}(\lambda_j) = & - \frac{1}{4\epsilon} \int d\mathbf{Q}_0 \cdots d\mathbf{Q}_P P(\mathbf{Q}_0, \cdots, \mathbf{Q}_P) \\ & G_\alpha(\mathbf{Q}_{P-j+1}) G_{\alpha'}(\mathbf{Q}_0) (Q_\alpha^{P-j+2} - Q_\alpha^{P-j}) (Q_{\alpha'}^1 - Q_{\alpha'}^P) \quad (28) \end{aligned}$$

where we have used a second-order Trotter split for the short imaginary time propagators, kept the lowest term in  $\epsilon^{-1}$ , and  $P(\mathbf{Q}_0, \cdots, \mathbf{Q}_P)$  is the regular sampling function used in the standard *cyclic* PIMC method (with  $\mathbf{Q}_{P+1} = \mathbf{Q}_0$ ).

As mentioned earlier, a *cyclic* PIMC expression of terms involving higher powers of momenta operators can be obtained following a similar derivation. The guiding lines in the derivation of the PIMC method are to avoid repeating derivatives of the same time slice, and to avoid higher derivatives of the coupling force. In some cases this is not achievable, and the statistical error along those imaginary time points will be larger.

## V. Results and Discussion

In this section we show that the PIMC method described in section IV provides a good estimate for the short-time expansion

coefficients ( $a$  and  $b$ ) of the Kubo transform of the force–force correlation function. The vibrational energy relaxation rate is obtained using eqs 10, 11, and 14. This method can be regarded as a “fully” quantum mechanical approach and thus is free of the limitations introduced in the classical and mixed quantum–classical approximations.<sup>7</sup>

We performed *cyclic* PIMC simulations for the model described in section II. We studied the vibrational relaxation rate as a function of the coupling strength  $\eta$  (see eq 6) and the vibrational frequency  $\omega_0$ . In performing the simulations the number of bath modes was chosen to be  $N_b = 100$ . This number of modes was sufficient to obtain converged vibrational energy relaxation rates. The number of Trotter slices was  $P = 100$ , and we employed the common staging algorithm<sup>28</sup> which leads to a greater mobility of the polymer chain. The number of staging moves varied between 3,000,000 and 10,000,000, and in each step we moved all of the beads (typically the acceptance ratio was above 0.5). This number of moves is required for two reasons: (a) the thermal average over momentum operators is more noisy and longer runs are needed to obtain a good estimate of the average, and (b) for simplicity we used the same Trotter slicing for all bath modes, and as a result the sampling of the low frequency modes is slower. The last limitation is typical only for the model at hand, and for a more realistic bath such as a Lennard-Jones bath, this would not be the case.

To obtain the coupling coefficients that would mimic the appropriate continuous spectral density in eq 5, we followed a standard procedure discussed by several authors.<sup>16,29</sup>  $J(\omega)$  was discretized evenly with an increment  $\delta\omega$ , and the coupling coefficients were calculated according to

$$g_\alpha^2 = \omega_\alpha J(\omega_\alpha) \delta\omega \quad (29)$$

The bath spectral density,  $J(\omega_\alpha)$ , is given in eq 6. In all of the calculations shown below, we choose the cutoff parameter in  $J(\omega)$  to be  $\omega_c = 0.3$ .

The results for the Kubo transform  $\psi_0$ ,  $\psi_2$ , and  $\psi_4$  are summarized in Table 1. In the PIMC simulations we have used the symmetry property  $\psi(\lambda) = \psi(\beta - \lambda)$ , and therefore calculated only one “surface term” ( $j = 0$ ). The numerical errors are less than a percent and are not shown in the table. Overall, we find very good agreement between the analytic moments and the numerical estimates based on the PIMC simulations. The agreement is excellent for  $\psi_0$  because it does not depend on momenta operators. As long as the coupling strength,  $\eta$ , is not too large, the agreement between the PIMC results and the analytic results for  $\psi_2$  and  $\psi_4$  is excellent. For the higher values of  $\eta$  the agreement is not as good. We attribute this deviation between the PIMC and analytical results to the finite Trotter slicing chosen, which for harmonic systems are known to produce systematic errors.<sup>26,30</sup> In summary, it is clear that the PIMC method developed here is capable of computing thermal averages over operators that include both positions and momenta.

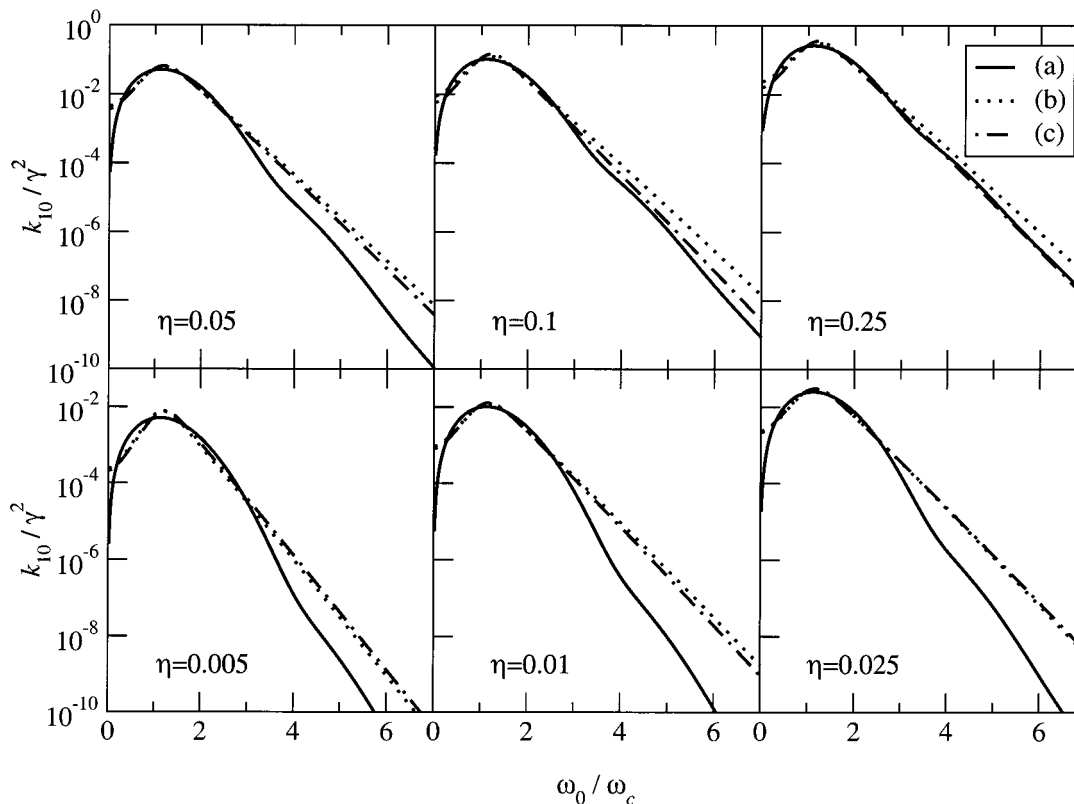
The good agreement for the Kubo transform of the short-time moments does not guarantee that the vibrational relaxation rate calculated using these moments will agree with the exact quantum mechanical rate. In Figure 1 we show a plot of the vibrational relaxation rate as a function of the vibrational frequency (in units of the cutoff frequency  $\omega_c$ ) for six values of the coupling strength  $\eta$ . Three plots are shown in each panel: (a) the exact quantum mechanical result (solid line), (b) the ansatz result using exact analytical moments (dotted line), and (c) the ansatz result using numerical moments obtained from the PIMC simulations (dashed–dotted line).



**TABLE 1: Summary of the Short-Time Moments of the Kubo Force–Force Correlation Function at  $\beta = 4^a$** 

$\eta$	analytic			numeric		
	$\psi_0$	$\psi_2$	$\psi_4$	$\psi_0$	$\psi_2$	$\psi_4$
0.250	0.01709	0.002332	0.0005448	0.01705	0.002411	0.0005350
0.100	0.006721	0.0009114	0.0002082	0.006763	0.0009544	0.0002069
0.050	0.003342	0.0004522	0.0001033	0.003309	0.0004552	0.0001017
0.025	0.001666	0.0002252	0.00005134	0.001671	0.0002220	0.00005071
0.010	0.0006654	0.00008987	0.00002070	0.0006659	0.00009046	0.00002027
0.005	0.0003325	0.00004490	0.000008971	0.0003322	0.00004798	0.00001011

<sup>a</sup> Note the excellent agreement between the analytic results and the PIMC simulations.



**Figure 1.** Plots of the vibrational energy relaxation rate as a function of the vibrational frequency for six values of the coupling strength  $\eta$ . (a) The exact fully quantum mechanical result (solid line). (b) The ansatz result with exact moments (dotted line). (c) The ansatz result with moments obtained from PIMC simulations (dotted-dashed line). The inverse temperature is  $\beta = 4$ .

We find that at low coupling strength and high vibrational frequencies the ansatz may differ from the exact quantum result by 2 orders of magnitude; however, because of the excellent agreement between the moments calculated analytically and numerically, the PIMC simulations agree with the ansatz over the entire frequency range shown. We believe that the use of a quantum mode coupling theory<sup>12</sup> (QMCT) will improve significantly the success of the short-time approach in those cases where damped coherent motion is important, namely in the low coupling regime.

At higher coupling strength the agreement between the ansatz and the exact result is improved; however, the agreement between the analytical and numerical moments is somewhat poorer, and as a result the PIMC simulation is no longer in perfect agreement with the analytic ansatz result. We note that for the cases studied here, the mixed quantum classical approach underestimates the rate by several orders of magnitude.<sup>7</sup>

Note that although a simple model has been used to study the efficiency of the quantum Monte Carlo method developed in this paper, the methodology is in no way confined to such simple models, because the quantum Monte Carlo procedure was performed numerically in a manner appropriate for systems

with realistic interactions. In fact, the harmonic system studied above is most likely *harder* to simulate than a more complex, realistic system. This is due to the well-known problems associated with the path integral simulation of harmonic environments.<sup>26,30</sup> Furthermore classical simulations on more realistic potentials suggest that the ansatz in eq 14 is likely to work *better* for the simple harmonic model studied here.

## VI. Conclusions

In this work we have considered the problem of calculating the vibrational relaxation rate of a molecule embedded in a condensed phase environment. The relaxation rate was formulated within the lowest order perturbation theory combined with the Kubo transform of the force–force correlation function. To avoid the limitations of the classical and mixed quantum-classical approximations, we have developed a fully quantum mechanical approach based on a short-time expansion of the Kubo correlation function. A simple analytical ansatz was used to obtain the correlation function at all times.

The expansion coefficients of the Kubo force–force correlation function depend on both position and momentum operators. Thus, the major goal of this work was to develop a path integral

Monte Carlo approach for these terms. We showed that the PIMC method outlined in section IV provides an accurate and robust method to obtain these thermal averages.

The PIMC method is general enough for use in the study of vibrational relaxation and other dynamical processes in condensed phases. For example, it may be shown<sup>12</sup> that the quantum equation of motion for the intermediate scattering function takes the form

$$\frac{d^2 F_\kappa(k, t)}{dt^2} + \omega_\kappa^2(k) F_\kappa(k, t) + \int_0^t d\tau K_\kappa(k, t - \tau) \frac{dF_\kappa(k, \tau)}{d\tau} = 0 \quad (30)$$

where  $F_\kappa(k, t) = \langle \hat{\rho}^\dagger \hat{\rho}(t) \rangle_\kappa$ ,  $\hat{\rho}$  is the quantum density operator  $\hat{\rho} = \sum_{i=1}^N \exp(i\mathbf{k} \cdot \mathbf{r}_i)$  and the subscript “ $\kappa$ ” denotes the fact that  $F_\kappa(k, t)$  is Kubo transform of the intermediate scattering function. The frequency factor,  $\omega_\kappa^2(k)$ , and the longitudinal memory function,  $K_\kappa(k, t - \tau)$  are described in ref 12.

The input required for this quantum generalization of the equation of the intermediate scattering function is simply the static averages that are already given in eq 30. This approach is generally quite successful in the classical limit, and has been applied to a wide variety of problems.<sup>11</sup> The extension to quantum mechanics is currently being developed to study quantum density fluctuations in low-temperature liquid *para*-hydrogen,<sup>12</sup> a system recently studied using an approximate method.<sup>31</sup> The ability to study quantum density fluctuations opens up the possibility to study a variety of interesting problems through the use of a *quantum* mode-coupling theory (QMCT).<sup>11,12</sup> For example, the density fluctuation spectrum obtained from a quantum viscoelastic treatment may be used to calculate the *long-time* behavior of the quantum force–force correlation function in a manner analogous to the classical mode-coupling approach.<sup>32</sup> The short-time behavior for the force–force correlation function may be obtained via the methods developed in this paper. The short and long-time regimes may be connected in a simple manner,<sup>11</sup> thus providing a more sophisticated approach to utilize the information provided by the PIMC methods discussed in this work. Such methods may also be used to study transport in quantum fluids, and even to develop a fully self-consistent quantum mode-coupling approach for studying density fluctuations. These topics will be the subject of future studies.

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## References and Notes

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