

On the calculation of time correlation functions in quantum systems: Path integral techniques^{a)}

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A Monte Carlo method for calculating quantum mechanical time correlation functions is presented. In this method the time correlation function is calculated at several values along the pure imaginary axis of the complex time plane such that $0 < it < \beta$, where $(\beta)^{-1}$ is the temperature of the system. Using the periodicity of the imaginary time correlation function, the real time behavior is inferred by analytic continuation. The method is used to calculate the absorption spectra of two model systems.

INTRODUCTION

Time correlation functions play a central role in the theory of dynamic processes in many-body systems.^{1,2} Transport properties, chemical reaction rate constants, spectroscopic line shapes, and neutron and light scattering spectra can all be related to well defined time correlation functions. In classical many-body systems, Hamiltonian dynamics or stochastic dynamics provide a basis for simulating time correlation functions. Unfortunately, the calculation of these functions in quantum systems is a formidable problem. In this letter we present a method for calculating time correlation functions in quantum and mixed quantum-classical systems based on path integral Monte Carlo techniques.

The method proposed springs directly from the Feynman path integral formulation of the canonical density matrix.^{3,4} The canonical equilibrium density matrix can be represented as a sum over all possible continuous paths obeying the appropriate boundary conditions. The weight of a given path is proportional to the exponential of the action along the path with a purely imaginary time. If the paths are discretized with P segments then the canonical density matrix can be written as a product of P terms each of which is the density matrix connecting the nearest segments. If P is sufficiently large then one can use the "short time" approximation for each of the P terms, and the partition function for the N particle quantum system can be identified as the partition function for the $N \times P$ classical particles.

Equilibrium properties of the quantum system can be obtained by solving the equivalent classical problem using standard numerical techniques (e. g., Monte Carlo). This procedure is guaranteed to yield the "exact" result in the limit $P \rightarrow \infty$. This formulation of the density matrix which tacitly assumes that paths that result from exchanging two or more particles can be ignored, has now been successfully applied to the calculation of the equilibrium properties of an electron immersed in helium⁵ and to the study of quantum effects in the structure of liquid water.⁶ Extending this procedure to calculate time correlation functions necessitates inclusion of paths with weights which are nonpositive in character. This arises because in the expression for time correlation functions both imaginary (thermal) times and real times are simultaneously present. The procedure we adopt enables us to simulate the many-body system using imaginary time

propagators only and the real time behavior can then be inferred by analytic continuation. This is very similar to the analytic continuation used to determine properties of real time Green's functions in N body quantum systems from the knowledge of the corresponding imaginary time (finite temperature) Green's functions.⁷ Recently, Chandler *et al.*⁸ have used this idea to investigate electronic absorption spectra of an impurity molecule in liquids within the context of the mean spherical approximation.

THEORY

It is well known from linear response theory that the response of a system to a weak external field can be expressed in terms of a time correlation function of a dynamical property of the system.¹ For example, the infrared absorption spectra is explicable in terms of the dipole-dipole correlation function, and the translational diffusion coefficient is related to the velocity autocorrelation function, etc. In this section we provide a general method to calculate the autocorrelation function $\langle A(t)A(0) \rangle$ where A can in principle be any quantum mechanical operator representing the N body system. To be specific, let us consider a many-body system consisting of N particles. The Hamiltonian for the system is taken to be

$$H = \sum_{i=1}^N \frac{p_i^2}{2m} + U(\mathbf{r}), \quad (1)$$

where p_i is the momentum of the i th particle, $U(\mathbf{r})$ is the potential of interaction between the N particles, and \mathbf{r} denotes the collection of all the coordinates of the many-body system. The one-sided time correlation functions are given by

$$F_{>}(t) \equiv \langle A(t)A(0) \rangle = \frac{\text{Tr}[e^{-\beta H} A(t)A(0)]}{\text{Tr} e^{-\beta H}}; \quad t > 0, \\ F_{<}(t) \equiv \langle A(0)A(t) \rangle = \frac{\text{Tr}[e^{-\beta H} A(0)A(t)]}{\text{Tr} e^{-\beta H}}; \quad t < 0, \quad (2)$$

where $Q \equiv \text{Tr} e^{-\beta H}$ is the canonical partition function. The Hermitean operator A can in principle be any dynamical operator representing the N -body system. The Fourier transform of $F_{>}(t)$ and $F_{<}(t)$ are defined by

$$F_{>}(\omega) = \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} e^{-i\omega' t} f_{>}(\omega'). \quad (3)$$

The cyclic invariance of the trace in Eq. (2) gives rise to the following boundary condition in time:

$$F_{>}(t) = F_{<}(t + i\beta\hbar). \quad (4)$$

Because of Eq. (4) the Fourier transforms satisfy detailed balance

$$f_{>}(\omega) = e^{\beta\hbar\omega} f_{<}(\omega). \quad (5)$$

It will now prove useful to introduce the imaginary part of the susceptibility $\chi''(\omega)$ which is defined as

$$\begin{aligned} \chi''(\omega) &= i[f_{>}(\omega) - f_{<}(\omega)] \\ &= i(1 - e^{-\beta\hbar\omega})f_{>}(\omega) \end{aligned} \quad (6)$$

in terms of which we can write $F_{>}(t)$ as

$$F_{>}(t) = \int_{-\infty}^{\infty} \frac{d\omega e^{-i\omega t}}{2\pi i} \frac{\chi''(\omega)}{(1 - e^{-\beta\hbar\omega})}. \quad (7)$$

It will now be shown that knowledge of $F_{>}(t)$ for $t = -i\lambda$ with $0 \leq \lambda \leq \beta\hbar$, is sufficient to determine the behavior of $F_{>}(t)$ for real time $t > 0$, and moreover to determine $\chi''(\omega)$. First note that $F_{>}(0) = F_{>}(-i\beta\hbar)$. This follows from the cyclic invariance of the trace. Thus on the interval $0 \leq \lambda \leq \beta\hbar$, $F_{>}(-i\lambda)$ can be expanded in the Fourier series,

$$F_{>}(t) = \frac{1}{(-i\beta\hbar)} \sum_n \exp(-iZ_n t) f(Z_n), \quad (8)$$

where $Z_n = 2\pi n/(-i\beta\hbar)$, $t = i\lambda$, and $0 \leq \lambda \leq \beta\hbar$. In order to relate the Fourier coefficients $f(Z_n)$ to $\chi''(\omega)$ the Fourier series [Eq. (8)] is inverted to give

$$f(Z_n) = \int_0^{-i\beta\hbar} dt \exp(+iZ_n t) F_{>}(t). \quad (9)$$

Substituting Eq. (7) into Eq. (9) and evaluating the t integral we obtain

$$f(Z_n) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{\chi''(\omega)}{(Z_n - \omega)}. \quad (10)$$

Knowledge of the Fourier $f(Z_n)$ coefficients determines $F_{>}(t)$ everywhere. From Eq. (10) it follows that $f(Z_n)$ is the analytic function:

$$\phi(Z) = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \frac{\chi''(\omega)}{(Z - \omega)} \quad (11)$$

evaluated at $Z = Z_n$.

It has thus been demonstrated that the task of calculating the Fourier transform of the correlation function has been reduced to evaluating the Fourier coefficients.

The procedure for finding $\chi''(\omega)$ from the Fourier coefficients is very simple. We merely analytically continue the Fourier coefficients evaluated at Z_n to all nonreal values of Z . Then $\chi''(\omega)$ is given by the discontinuity across the real axis, i. e.,

$$\chi''(\omega) = i[f(\omega + i\epsilon) - f(\omega - i\epsilon)]. \quad (12)$$

We now address the evaluation of the Fourier coefficients given by Eq. (9). Let λ denote a point on the pure imaginary axis of the complex time plane such that $0 \leq \lambda < \beta\hbar$. The Fourier coefficient evaluated at Z_n can be written as

$$f(Z_n) = \frac{1}{i} \int_0^{\beta\hbar} d\lambda e^{+Z_n \lambda} F_{>}(-i\lambda), \quad (13)$$

where

$$F_{>}(-i\lambda) \equiv \frac{1}{Q} \text{Tr} \rho(\beta - \lambda/\hbar) A \rho(\lambda/\hbar) A. \quad (14)$$

Here $\rho(\gamma) = e^{-\gamma H}$ is the canonical density operator at reciprocal temperature γ . This can be expressed in the position representation as

$$\begin{aligned} F_{>}(-i\lambda) &= \frac{1}{Q} \int \cdots \int dq_1 dq'_1 dq_2 dq'_2 \rho(q_1, q'_1; \beta - \lambda) \\ &\quad \times \langle q'_1 | A | q_2 \rangle \rho(q_2, q'_2; \lambda) \langle q'_2 | A | q_1 \rangle, \end{aligned} \quad (15)$$

where

$$\rho(q_1, q'_1; \gamma) \equiv \langle q_1 | e^{-\gamma H} | q'_1 \rangle.$$

The density matrices $\rho(q_1, q'_1; \beta - \lambda)$ and $\rho(q_2, q'_2; \lambda)$ can now be represented as path integrals in the usual way using L and P discrete points, respectively.

In particular, $\rho(q_1, q'_1; \beta - \lambda)$ can be written as

$$\begin{aligned} \rho(q_1, q'_1; \beta - \lambda) \\ = \int dr_2 \cdots \int dr_L \sum_{i=1}^L \langle r_i | \exp[-(\beta - \lambda)H/L] | r_{i+1} \rangle, \end{aligned} \quad (16)$$

where $r_1 \equiv q_1$ and $r_{L+1} \equiv q'_1$. Similarly, $\rho(q_2, q'_2; \lambda)$ is given by

$$\rho(q_2, q'_2; \lambda) = \int dr'_2 \cdots \int dr'_P \prod_{i=1}^P \langle r'_i | e^{-\lambda H/P} | r'_{i+1} \rangle, \quad (17)$$

where $r'_1 \equiv q_2$ and $r'_{P+1} \equiv q'_2$.

If L and P are made large enough so that $(\beta - \lambda)/L$ and λ/P are sufficiently small the usual high temperature approximation for $\langle r_i | \exp[-(\beta - \lambda)H/L] | r_{i+1} \rangle$ and $\langle r'_i | \exp[-\lambda H/P] | r'_{i+1} \rangle$ can be used, i. e.,

$$\begin{aligned} \langle r_i | \exp[-(\beta - \lambda)H/L] | r_{i+1} \rangle &= \left[\frac{mL}{2\pi\hbar^2(\beta - \lambda)} \right]^{1/2} \\ &\quad \times \exp \left[- \frac{mL(r_i - r_{i+1})^2}{2\hbar^2(\beta - \lambda)} + \frac{(\beta - \lambda)}{L} U(r_i) \right] \end{aligned} \quad (18)$$

and

$$\langle r'_i | e^{-\lambda H} | r'_{i+1} \rangle = \left[\frac{mP}{2\pi\hbar^2\lambda} \right]^{1/2} \exp \left[- \frac{mP(r'_i - r'_{i+1})^2}{2\hbar^2\lambda} + \frac{\lambda}{P} U(r'_i) \right], \quad (19)$$

substituting Eqs. (16)–(19) into Eq. (15) yields an explicit expression for $F_{>}(-i\lambda)$ which can be interpreted as two classical polymers consisting of L and P segments, respectively, one of which is at temperature $(\beta - \lambda)^{-1}$ and the other at temperature λ^{-1} . Furthermore, the ends of these polymers are connected by matrix elements of the operator A .

There are two possible methods for evaluating Eq. (14).

(a) Direct Monte Carlo simulation for different values of λ .

(b) Numerical matrix multiplication of the short time expansion.⁹

Method (a) is more easily applied to many-body systems whereas method (b) provides a very rapid and accurate approach to one quantum particle embedded in a classical bath.

The procedure may be summarized as follows:

(1) Evaluate $F_{\gamma}(t)$ along the pure imaginary time axis between the intervals

$$0 \leq it \leq \beta \hbar .$$

(2) Calculate the Fourier coefficients using Eqs. (13) and (14).

(3) The Fourier transform of the correlation function may be obtained using Eqs. (11) and (12).

NUMERICAL METHOD FOR ANALYTIC CONTINUATION

A natural method for performing a numerical analytic continuation is to use the Padé approximant scheme. If the values of $f(Z_n) [\equiv f_n]$ are known for $n=1$ to $n=N+M+1$ values, then the function $f(Z)$ can be represented by the quotient

$$f(Z) = [N, M] = \frac{\sum_{i=0}^M b_i p_i(Z)}{q_0(Z) + \sum_{i=1}^N c_i q_i(Z)} . \quad (20)$$

The coefficients b_i and c_i can be calculated from $f(Z)$ evaluated at $(N+M+1)$ points. The functions $p_i(Z)$ and $q_i(Z)$ are chosen appropriately for the problem under consideration. Using the eigenstates of the Hamiltonian (only bound states) it can be shown that $f_{\gamma}(\omega)$ is a meromorphic function of ω with simple poles at the excitation frequencies of the system which are connected by the dynamical operator. This suggests that we choose $p_i(Z) = q_i(Z) = Z^i$. Without loss of generality we set $q_0(Z)$ to unity. By virtue of the absolute convergence of canonical averages the integral of the absolute value of $\chi''(\omega)$ exists and from Eq. (6) it can be concluded that: (i) $\Phi(Z)$ is analytic off the real axis; (ii) $\Phi(Z) \sim 1/Z$ for large Z , where $\Phi(Z)$ is defined by Eq. (11). Conditions (i) and (ii) specify the unique analytic condition. The order of the Padé approximant consistent with the "sum rule" given by condition (ii) is $[N, N-1]$. With the choice of functions for $p_i(Z)$, $q_0(Z)$, and $q_i(Z)$ the unknown coefficients $\{b_i, c_i\}$ may be calculated by solving an algebraic equation. Knowledge of the coefficients enables us to compute $\chi''(\omega)$ using Eq. (12).

APPLICATIONS

In order to assess the overall numerical efficacy of the method proposed here, we have calculated the absorption spectrum of an oscillator when irradiated with light. The dynamic quantity that is needed to obtain the absorption spectra is $\langle \mu(0)\mu(t) \rangle$ where μ is the dipole moment. For an oscillator μ is taken to be proportional to q where q is the displacement from the equilibrium bond length. This particular choice of μ was made for convenience and it is worth noting that one can in practice use any arbitrary functional dependence of μ on q . From linear response theory it follows that the absorption line shape is proportional to $\hat{I}(\omega)$ where

$$\hat{I}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} \langle q(0)q(t) \rangle \equiv f_{\gamma}(\omega) . \quad (21)$$

Before describing the calculation of $\hat{I}(\omega)$ for two exactly soluble models of the quantum oscillator, it is useful to list certain numerical aspects of the method that are relevant for the computation of any autocorrelation function.

(a) Due to the trace invariance of the averages we are performing, $F_{\gamma}(-i\lambda)$ [cf. Eq. (15)] is symmetric about $\lambda = \beta \hbar / 2$. Consequently, one needs to calculate $F_{\gamma}(-i\lambda)$ only over the range of $0 \leq \lambda \leq \beta \hbar / 2$.

(b) When the matrix element of the dynamical variable in the position representation and the semiclassical approximation for ρ [Eqs. (18) and (19)] are substituted into Eq. (15) an explicit expression for $F_{\gamma}(-i\lambda)$ is obtained. For a given potential of interaction and a given temperature (β^{-1}), there are two parameters L and P involved in the equation for $F_{\gamma}(-i\lambda)$, where L and P are the number of discrete points constituting the two polymer "segments" at inverse temperatures $(\beta - \lambda)$ and λ , respectively. The values of L and P have to be large enough so that the semiclassical approximations given by Eqs. (18) and (19) are valid.

(c) For a given value of L , P , and λ , Eq. (15) can be evaluated by the standard Metropolis MC algorithms. Since it is necessary to evaluate $g_{\gamma}(\lambda)$ [cf. Eq. (15) for a sufficiently large number of values of λ], it is perhaps worthwhile looking for a more accurate short time approximation. In an attempt to accelerate the convergence of MC algorithms we tried an improved short time approximations based on the Wigner-Kirkwood expansion, namely

$$\rho(x_t, x_{t+1}; \epsilon) = \left[\frac{m}{2\pi \hbar^2 \epsilon} \right]^{1/2} \exp \left\{ - \left[\frac{\epsilon}{2} V(x_t) + \frac{m(x_t - x_{t+1})^2}{2\hbar^2 \epsilon} + \frac{\epsilon}{2} V(x_{t+1}) + \frac{\epsilon \hbar^2}{24m} V''(x_t) \right] \right\} . \quad (22)$$

It was found that the convergence of $F_{\gamma}(-i\lambda)$ for the dynamical operator \hat{q} improved dramatically. We note that one can use more accurate expressions for $\rho(x_t, x_{t+1}; \epsilon)$ than suggested by Eq. (22). For example, the potential can be expanded in the neighborhood of an arbitrary point $\bar{x} \in (x_t, x_{t+1})$ e. g., $\bar{x} = (x_t + x_{t+1})/2$ up to second order. Now the path integral within a segment can be evaluated as

$$\rho(x_t, x_{t+1}; \epsilon) = \left[\frac{m\omega_0}{2\pi \hbar \sinh(\epsilon \hbar \omega_0)} \right]^{1/2} \times \exp \left\{ - \epsilon \left[V(\bar{x}) + \frac{(V'(\bar{x}))^2}{2V''(\bar{x})} \left(\frac{\tanh \frac{\epsilon \hbar \omega_0}{2}}{\frac{\epsilon \hbar \omega_0}{2}} - 1 \right) \right] \right\} \times \exp \left\{ \frac{-m\omega_0}{2\hbar} (x_t - x_{t+1})^2 \coth \frac{\epsilon \hbar \omega_0}{2} \right\} , \quad (23)$$

where

$$\omega_0 = [V''(\bar{x})/m]^{1/2} .$$

It should be noted that for small ϵ , Eq. (23) reduces to Eq. (22). Although we did not explore Eq. (23), it might be necessary to use these equations $\rho(x_t, x_{t+1}; \epsilon)$ if one

is dealing with complex condensed phase systems.

(d) Finally we remark on the convergence of Padé approximants to accomplish the task of analytic continuation of the Fourier coefficients. The Padé approximant attempts to approximate Eq. (6) by

$$\Phi(Z) = \sum_r \frac{\gamma_r}{(Z - \omega_r)}, \quad (24)$$

where the excitation frequencies $\{\omega_r\}$ of the system are given by the zeros of the denominator of Eq. (20) and the residues $\{\gamma_r\}$ are evaluated at these frequencies. What are needed therefore are very accurate values of the Fourier coefficients so that one needs to evaluate $F_{\lambda}(-i\lambda)$ on a reasonably fine grid to high precision. Our experience leads us to believe that the error bars in the reported simulation should not exceed 5%.

CASE A [LINEAR HARMONIC OSCILLATOR (LHO)]

We now consider the evaluation of $\hat{I}(\omega)$ for a harmonic oscillator of mass m and frequency ω_0 . The expression for $F_{\lambda}(-i\lambda)$ obtained by substituting the matrix element of \hat{q} and the potential $V(q) = m\omega_0^2 q^2/2$ yields a $(N-1)$ dimensional integral involving a multivariate Gaussian. For our choice of $\beta = 2.993/\hbar\omega_0$ it was found that $L = P = 10$ was sufficient to get accurate values for $F_{\lambda}(-i\lambda)$ for all values of λ . The evaluation of $F_{\lambda}(-i\lambda)$ for a given set of parameters can be done analytically and this can be compared to the results of the simulation directly. It was found that on the average 2×10^5 to 3×10^5 passes were required to obtain satisfactory error bars. The simulations were performed at selected values of λ in the range $0 \leq \lambda \leq \beta\hbar/2$. Cubic spline interpolation was used to calculate $F_{\lambda}(-i\lambda)$ at other values of λ . The Fourier coefficients were obtained using the Filon quadrature scheme.¹¹ The results of the calculation and the associated intensities are presented in Table I.

The intensity associated with a transition is obtained by using the equation

$$I(\omega_r) = \frac{2\pi\gamma_r}{[\exp(\beta\hbar\omega_r) - 1]}, \quad (25)$$

where γ_r is the residue evaluated at ω_r using the coefficients of the $[N, N-1]$ Padé approximant. It is encouraging to note that both the frequency of the transition and the corresponding intensity converge very rapidly to the exact answer with increasing N .

TABLE I. Excitation frequency and intensity of the dipole spectrum of the LHO by Padé continuation.^a

$[N, N-1]$	ω_0	$I(\omega_0)$
1	0.013 6055	6.872 80(-3)
2	0.013 6056	6.872 89(-3)
3	0.013 6056	6.872 89(-3)
Exact	0.013 6056	6.872 89(-3)

^aAll values are in a.u.

TABLE II. Excitation frequencies and the corresponding intensities of the dipole spectrum of the Morse oscillator obtained by Padé continuation.^a

$[N, N-1]$	ω_{10}	ω_{12}	ω_{13}	ω_{20}	ω_{30}
3	1.48(-2)	1.17(-2)	...	3.03(-2)	4.81(-2)
4	2.57(-2)	1.82(-2)	2.72(-2)	4.33(-2)	5.42(-2)
5	2.58(-2)	1.82(-2)	2.78(-2)	4.34(-2)	5.42(-2)
6	2.58(-2)	1.82(-2)	2.72(-2)	4.33(-2)	5.42(-2)
7	2.58(-2)	1.81(-2)	2.83(-2)	4.33(-2)	5.42(-2)
Exact	2.53(-2)	1.81(-2)	2.89(-2)	4.34(-2)	5.42(-2)
$[N, N-1]$	$I(\omega_{10})$	$I(\omega_{12})$	$I(\omega_{13})$	$I(\omega_{20})$	$I(\omega_{30})$
3	8.08(-2)	4.67(-2)	...	3.29(-3)	7.38(-4)
4	1.05(-2)	5.71(-3)	9.67(-5)	6.86(-4)	7.14(-5)
5	1.04(-2)	4.22(-3)	1.07(-4)	6.75(-4)	7.09(-5)
6	1.05(-2)	4.22(-3)	1.32(-4)	5.26(-4)	7.11(-5)
7	1.05(-2)	4.32(-3)	1.35(-4)	5.26(-4)	7.05(-5)
Exact	1.03(-3)	4.17(-3)	1.49(-4)	5.00(-4)	6.58(-5)

^aAll values are in a.u.

CASE B (MORSE OSCILLATOR)

The second model was the Morse oscillator with $V(q)$ given by

$$V(q) = D_e \{1 - \exp[-\alpha(q - q_e)]\}^2, \quad (26)$$

with $D_e = 0.073 15 E_h$, $q_e = 4.308 55 a_0$, and $\alpha = 2.566 607 a_0^{-1}$. The mass of the oscillator was set equal to $m = 911.413$ a.u. The parameters were chosen to give a total of four bound states. This could conceivably be a model for a weak chemical bond like that found in a van der Waals molecule. The temperature of the system was set at $T = (\hbar\omega_0/3.02 k_B)$ where k_B is the Boltzmann constant. In order to obtain reasonably accurate values for $F_{\lambda}(-i\lambda)$ in the range $0 \leq \lambda \leq \beta\hbar/2$, we performed simulations for over 30 values of λ . For each λ the values of L , P and the number of passes were adjusted to obtain satisfactory error bars. Typically, the number of discrete points in the two polymers, i.e., $L + P$ varied between 50 to 60 and the number of passes required varied from 2.5×10^5 to 4.0×10^5 . The resulting curve was smoothed out to remove spurious fluctuations and cubic spline extrapolation was used to obtain $F_{\lambda}(-i\lambda)$ at other values of λ . The Fourier coefficients were obtained as before and the analysis of the excitation frequencies proceeds as described in the discussion of the LHO. The transitions from the first excited state to states 2 and 3 were found by subtracting the contribution from the $1-0$ transition and fitting the resulting function to a Padé approximant of suitable order. We note here that in the process the locations of the residues and the poles of the other transitions were unaffected. The results of our calculation are presented in Table II. The convergence of the excitation frequencies with respect to the order of the Padé approximant used to the exact result is indeed dramatic. Although all possible transitions are connected by the dipole moment operator we do not observe transition from the $2 \rightarrow 3$ level. The reason for this is simply that the levels 2, 3 are not highly populated at this temperature. Therefore, the intensities associated with these transitions are expected to be very weak and

are thus swamped by the strong transitions. Similar remarks apply to the question of convergence of the intensities.

It should be emphasized that increasing the order of the Padé approximant beyond some number does not automatically ensure better convergence—in fact the opposite may be true. Unless the input is known extremely accurately the matrix that is being inverted to obtain the unknown coefficients in the Padé combination becomes singular and causes numerical problems. Since there are normal numerical uncertainties in our calculation the input to the Padé combination is not very accurate and this causes the singularity problem associated with the inversion of the matrix. Problems of this nature are well recognized by practitioners of Padé summation techniques and for a very detailed discussion the reader is referred to the excellent chapter by Langhoff and Karplus in Ref. 12. Despite this it is encouraging that we have been able to calculate the excitation frequencies and the associated intensities for both oscillator models.

CONCLUSION

In this paper we have developed a numerical method for calculating time correlation functions in quantum mechanical systems. This method should be useful for theoretical studies of molecular spectroscopy and chemical kinetics in the condensed phase, where the equivalent polymeric classical systems can be simulated. It is anticipated that this method will be most useful if one is interested in dynamical properties of a quantum impurity immersed in a bath of classical particles and if the motion associated with the quantum particle is in some sense much faster than the classical motion. In such a situation one can profitably employ the Born–Oppenheimer approximation and solve the quantum dynamics for each fixed classical configuration. Finally the quantum dynamics can be obtained by averaging over all possible classical configurations. It is fortunate that many interesting physical situations do indeed satisfy these conditions, e. g., the mobility of an

electron or proton in an atomic or molecular matrix (the quantum Lorentz gas), solvent effects on tautomerization reactions, and electron transfer reactions. Simulations of such systems are presently in progress.

Note added in proof. Recently we received a preprint: Quantum Mechanical Rate Constants for Biomolecular Reactions by W. H. Miller, S. D. Schwartz, and J. W. Troup in which a path integral expression for the time correlation function describing dissociation was evaluated by analytical continuation in the complex time plane. This method is not equivalent to the method proposed here.

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