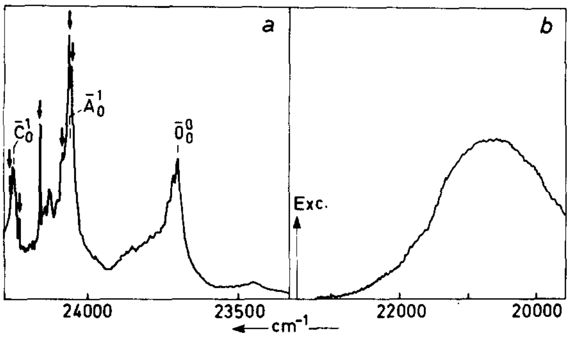

FIG. 2. Low frequency part of the fluorescence excitation spectrum and fluorescence spectrum of the perylene-DMA complex.

sition and almost structureless elsewhere are superimposed at this background (Fig. 2). Under excitation of the background or of the structured spectrum a characteristic exciplex emission is observed: a broad ($\delta\nu = 2500$ cm^{-1}), structureless band with $\nu_{\max} = 20\,900$ cm^{-1} for perylene-DMA and 22 400 cm^{-1} for anthracene-DMA, i.e., blue shifted by ~ 1500 cm^{-1} with respect to alkane solutions[6] and—in the latter case—nearly the same as that of the isolated anthracene-$(CH_2)_n$-DMA intramolecular exciplex.[7] The fluorescence lifetimes of complexes are much longer than those of bare molecules (~ 10 and ~ 100 ns for perylene and its complex).

The results may be explained by assuming existence of two closely spaced electronic states of the AD complex (van der Waals in its ground state): a locally excited A^*D state (A^* excited state perturbed by van der Waals interaction stronger than in the ground state) and a charge-transfer (CT) A^-D^+ state. In the TEA complexes the A^*D state is the lowest one giving origin to the structured emission similar to that of A^*; the quasicontinuous absorption in the high-frequency range may be due to the CT state. In DMA complexes the CT state is the lowest and the level broadening in the A^*D spectrum is obviously due to the rapid electronic relaxation to the A^-D^+ state followed by the exciplex emission.

Three points merit attention:

(i) A completely diffuse absorption to the nondissociative CT state of a cold complex (already reported in Ref. 2) is surprising. It may be due to an exceptionally strong electron-vibration coupling and to a very rapid vibrational redistribution.

(ii) The vibrational redistribution in the perylene-TEA complex is relatively slow ($t_{\text{red}} > 5$ ps from the absence of line broadening) although its onset is drastically lowered with respect to the free molecule (from 1700[5] to below 300 cm^{-1}).

(iii) The vibrational predissociation of complexes above the dissociation threshold is also very slow (insignificant for short-lived TEA complexes, more pronounced for long-lived DMA ones).

The work is being continued and complete results will be published elsewhere.

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Time correlation functions in quantum systems

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Thirumalai and Berne[1] have shown that correlation functions in Euclidean time determined by Monte Carlo techniques can be analytically continued in Laplace space to obtain information about real time dynamics. The advantage of this methodology is that it allows use of classical Monte Carlo methods. Other methods have also been tried.[2,3]

In this comment we present a rather straightforward method for evaluating time correlation functions using path integral techniques. This method does not involve analytical continuation and it also lends itself to classical Monte Carlo methods. We apply it to the evaluation of dynamics of a double well system. Direct application to this of the short time propagation using the numerical matrix multiplication shows that this method is remarkably stable and accurate. Solvent effects are treated in a forthcoming paper.[4]

Consider the two functions

$$C_{AB}(t) = Q^{-1}\,\mathrm{Tr}[e^{-\beta H}\mathrm{A}e^{iHt}\mathrm{B}e^{-iHt}] \tag{1}$$

and

$$G_{AB}(t) = Q^{-1}\,\mathrm{Tr}\,\mathrm{A}e^{-H\tau}\,\mathrm{B}e^{-H\tau^*}, \tag{2}$$

where t is the Minkowski (real) time and $\tau = (\beta\hbar/2 - it)$ is a complex time. It is easily shown[2] that $\overline{G}_{AB}(\omega) = \exp(-\beta\hbar\omega/2)\overline{C}_{AB}(\omega)$ so that $C_{AB}(t)$ can be obtained from

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$G_{AB}(t)$. If A and B are position dependent operators, then in the coordinate representation

$$G_{AB}(t) = Q^{-1} \int dx \int dx' \, A(x) B(x') |\langle x | e^{-H\tau} | x' \rangle|^2 \quad (3)$$

so that we need only determine the Green's operator $\langle x | e^{-H\tau} | x' \rangle$. Only for autocorrelation functions is $G_{AA}(t)$ an even real function of time. In a previous paper[5] we showed how such operators can be evaluated using numerical matrix multiplication together with the short time approximations.

As an example, we calculate the dipole–dipole correlation function of a proton moving in a bistable potential given by Eq. (8) of Ref. 5. It is important to note that we are implicitly treating all bound states. This corresponds to proton tunneling in H_2O_2 at a temperature of 10 K. For the dipole operator we take $\mu(q) = \mu_0 \tanh(\alpha q)$, where $\mu_0 = 1$ and $1/\alpha = 0.1$ a.u. is much smaller than the width of the potential. If only the two lowest states were to contribute at 10 K, $G_{\mu\mu}(t) = Q^{-1} |\mu_{12}|^2 \exp[-\beta(E_0 + E_1)/2] \cos[(\Delta\omega)t]$, where μ_{12} is the transition moment, and $\Delta\omega = (E_1 - E_0)/\hbar$ is the tunnel splitting. In Fig. 1 we compare the simulation using NMM with ($n = 6,9,11$) with the two state approximation. This is equivalent to a discretized path integral in the primitive algorithm with $P = 64$, 512, and 2048, respectively. We note that a large chain is required for good convergence. The time corresponds to eight periods. It is important to note that a similar evaluation of $C_{\mu\mu}(t)$ [cf. Eq. (1)] leads to numerical instabilities even at short times. Because $\bar{C}(\omega) = \bar{G}(\omega) e^{\beta\hbar\omega/2}$, it is possible that small errors in $\bar{G}(\omega)$ at high frequencies will be amplified by $\exp \beta\hbar\omega/2$, this has yet to be studied.

This study shows that it would be inadvisable to use Monte Carlo methods to evaluate $C_{\mu\mu}(t)$. On the other hand such methods should be stable for the direct evaluation of $G_{\mu\mu}(t)$. This can be appreciated by studying the explicit path integral form of $G_{AB}(t)$:

$$G_{AB}(t) = \int dx_1 \dots dx_{2P} \, F(x_1 \dots x_{2P}) P(x_1, \dots, x_{2P}), \quad (4a)$$

where P is the Monte Carlo sampling function

$$P(x_1 \dots x_{2P}) = \left(\frac{m^2 P^2}{\Pi^2 (\beta^2 + 4t^2)} \right)^{Pd/2} \exp\left[-\beta \sum_{j=1}^{2P} \times \left\{ \frac{mP}{(\beta^2 + 4t^2)} (x_j - x_{j+1})^2 + \frac{1}{2P} V(x_j) \right\} \right] \quad (4b)$$

and where F is

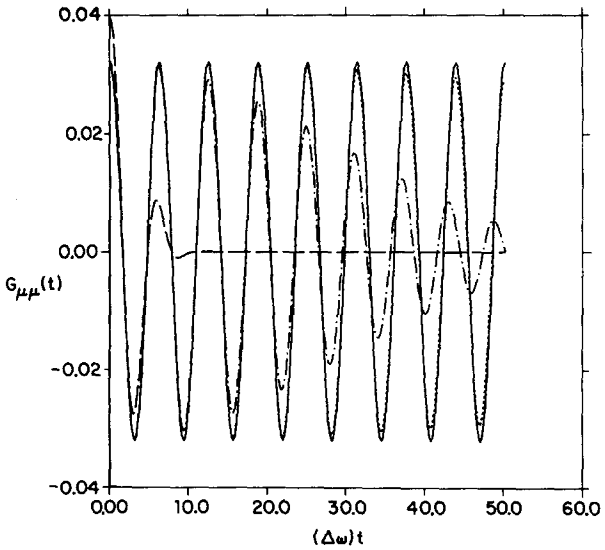

FIG. 1. The correlation function $G_{\mu\mu}(t)$ vs time for protonic tunneling in H_2O_2 at $T = 10$ K. The solid curve represents the analytical time dependence determined using the two lowest states (frequency splitting, $\Delta\omega = 4.87$ K). The curves ---, -----, and ···· represent $G_{\mu\mu}(t)$ calculated using discretized path integrals with $P = 64$, 512, and 2048, respectively. The time is given in reduced units of $(\Delta\omega)t$, and $G_{\mu\mu}(t)$ is given in atomic units.

$$F(x_1 \dots x_{2P}) = A(x_1) B(x_{P+1}) \exp\left(-it \sum_{j=1}^{P} \times \left\{ \frac{2MP}{(\beta^2 + 4t^2)} [(x_j - x_{j+1})^2 - (x_{j+P} - x_{j+P+1})^2] + \frac{1}{P} [V(x_j) - V(x_{j+P})] \right\} \right). \quad (4c)$$

The basic approach is to sample the configurations $(x_1 \dots x_{2P})$ from Eq. (4b) and average $F(x_1 \dots x_{2P})$ over these configurations. Because F involves a phase factor that depends on the differences between functions of the sampled configurations it is expected that cancellation will result and that the average will be much more stable than would be the case for a direct attack on $C_{AB}(t)$. This is borne out in the NMM study given in Fig. 1.

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