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Quantum reaction rates and sampling of quantum equilibrium structure

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Quantum time correlation functions obtained from the linear response theory are defined in terms of a scalar product involving the Kubo transform.[1] This form of the scalar product also insures that the nonequilibrium average of the random force fluctuations corresponding to an observable vanish so that the macroscopic law is obtained on long distance and time scales and the Onsager regression hypothesis is satisfied. For example, consider a reaction $A \rightleftharpoons B$ where species A and B are defined microscopically by operators $\hat{N}_{A,B}$, respectively. The time dependent quantum forward reaction rate is given by the Kubo-transformed reactive flux correlation function,[2] $k(t)n_A^{\mathrm{eq}}=-\langle\dot{\hat{N}}_A;\hat{N}_B(t)\rangle$, where n_A^{eq} is the equilibrium density of species A. The rate constant is given by $k=\lim_{t\to\infty}k(t)$. Introducing Wigner transforms, we can write an alternative but equivalent form of $k(t)$ as

$$k(t)n_A^{\mathrm{eq}}=\int d\mathcal{X}N_B(\mathcal{X},t)\bar{W}_A(\mathcal{X},0), \tag{1}$$

where $\mathcal{X}=(\mathcal{R},\mathcal{P})$ denotes phase space variables and $N_B(\mathcal{X},t)$ is the Wigner transform of $\hat{N}_B(t)$. The spectral density function $\bar{W}_A(\mathcal{X},0)$ describes the quantum equilibrium structure and it is defined by $\bar{W}_A(\mathcal{X},0)=\beta^{-1}\int_0^\beta d\lambda W_A(\mathcal{X},i\hbar\lambda)$, where

$$\begin{aligned}W_A(\mathcal{X},t)=&\int d\mathcal{X}'(-\dot{\hat{N}}_A(\mathcal{X}'))\int d\mathcal{Z}d\mathcal{Z}'e^{-(i/\hbar)(\mathcal{P}\mathcal{Z}+\mathcal{P}'\mathcal{Z}')}\\&\times\left\langle\mathcal{R}+\frac{\mathcal{Z}}{2}\middle|e^{-\beta\hat{H}-(i/\hbar)\hat{H}t}\middle|\mathcal{R}'-\frac{\mathcal{Z}'}{2}\right\rangle\\&\times\left\langle\mathcal{R}'+\frac{\mathcal{Z}'}{2}\middle|e^{(i/\hbar)\hat{H}t}\middle|\mathcal{R}-\frac{\mathcal{Z}}{2}\right\rangle\frac{1}{(2\pi\hbar)^{2\nu}Z_Q},\end{aligned} \tag{2}$$

with $\beta=1/k_BT$, ν is the coordinate space dimension of the system, and Z_Q is the partition function. One of the difficulties in computing the reaction rate arises from the form of $\bar{W}_A(\mathcal{X},0)$. Since $W_A(\mathcal{X},i\hbar\lambda)$ is already a very complicated function, the integration required to compute $\bar{W}_A(\mathcal{X},0)$ adds considerably to the computational effort. Even for a single harmonic oscillator, $\bar{W}_A(\mathcal{X},0)$ cannot be obtained in a closed analytic form. We have previously shown[3] that $\bar{W}_A$ may be approximated by $\bar{W}_A(\mathcal{X},0)=W_A(\mathcal{X},i\hbar\beta/2)+\mathcal{O}(\beta^2)$.

If one is simply interested in the rate constant, and not the time evolution of the correlation function, then we may make use of the fact that the rate constant can also be expressed as $k=\lim_{t\to\infty}k^*(t)$ where $k^*(t)$ is defined without the Kubo transform as $k^*(t)n_A^{\mathrm{eq}}=-\langle\dot{\hat{N}}_A\hat{N}_B(t)\rangle$. This result follows from the relation between the Fourier transforms of the Kubo-transformed correlation function and the quantum canonical average in the zero frequency limit.[1] The analog of Eq. (1) for $k^*(t)$ is $k^*(t)n_A^{\mathrm{eq}}=\int d\mathcal{X}N_B(\mathcal{X},t)W_A(\mathcal{X},0)$. Since this expression only requires a knowledge of $W_A(\mathcal{X},0)$, instead of the more complex expression $\bar{W}_A(\mathcal{X},0)$ or its approximate form $W_A(\mathcal{X},i\hbar\beta/2)$, it is far easier to compute.

Before considering a more general system-bath problem, it is instructive to compare $\bar{W}_A(x,0)$, $W_A(x,i\hbar\beta/2)$, and $W_A(x,0)$ for a simple parabolic barrier crossing model with phase space coordinates $x=(r,p)$ and barrier frequency ω. For this system we can obtain the analytic form of $W_A(x,t)$ from Eq. (2) as follows:

$$\begin{aligned}W_A(x,t)Z_Q=&\left(\frac{m\omega}{\pi\hbar c_1}\right)^{3/2}\frac{1}{2m\sin u}\left(\frac{pc_2}{m\omega}-rc_3\right)\\&\times\exp\left[-\frac{m\omega}{\hbar c_1}\left\{\left(\frac{p}{m\omega}\right)^2-r^2+\left(rc_2-\frac{pc_3}{m\omega}\right)^2\right\}\right],\end{aligned} \tag{3}$$

where $u\equiv\beta\hbar\omega/2$, $c_1=\cot u$, $c_2(t)=c_1\cosh\omega t-i\sinh\omega t$, and $c_3(t)=c_1\sinh\omega t-i\cosh\omega t$. Since we cannot integrate $W_A(x,i\hbar\lambda)$ analytically to obtain $\bar{W}_A(x,0)$, the exact spectral density function and time-dependent rate $k(t)$ can be obtained only numerically. From Eq. (3), both $W_A(x,i\hbar\beta/2)$ and $W_A(x,0)$ are easily determined and can be used to compute $k(t)$. Substituting $W_A(x,i\hbar\beta/2)$ into Eq. (1), we can obtain Eq. (3.6) of Ref. 4 and using $W_A(x,0)$ we obtain $\mathrm{Re}[k(t)Z_R]=(\omega/4\pi\sin u)[(f_1\sqrt{f_3+f_2}+\sqrt{f_3-f_2})/2f_3\sqrt{f_1}]$, where $f_1(t)=\cot u\tanh\omega t$, $f_2(t)=\cot 2u\tanh\omega t$, $f_3^2(t)=f_2^2(t)+1$, and $Z_R\equiv n_A^{\mathrm{eq}}Z_Q$. Since $W_A(x,0)$ is complex, $\mathrm{Im}[k(t)Z_R]$ is not zero at finite t but it vanishes in the $t\to\infty$ limit.

In Fig. 1, one can see that the shape of $W_A(x,i\beta\hbar/2)$ is Gaussian and is most convenient for the sampling of the initial values of r and p, while $\mathrm{Re}W_A(x,0)$ has the most complicated structure making sampling more difficult. This figure also shows the time-dependent rate coefficient $k(t)Z_R$ calculated using these three spectral density functions. Despite different time dependence of these estimates, all three predict the same rate constant, kZ_R. The time dependent rate coefficient computed using $\mathrm{Re}W_A(x,0)$ converges to kZ_R rapidly, although it does not start at zero.

These considerations can be extended to more general situations and we next consider the calculation of the reac-

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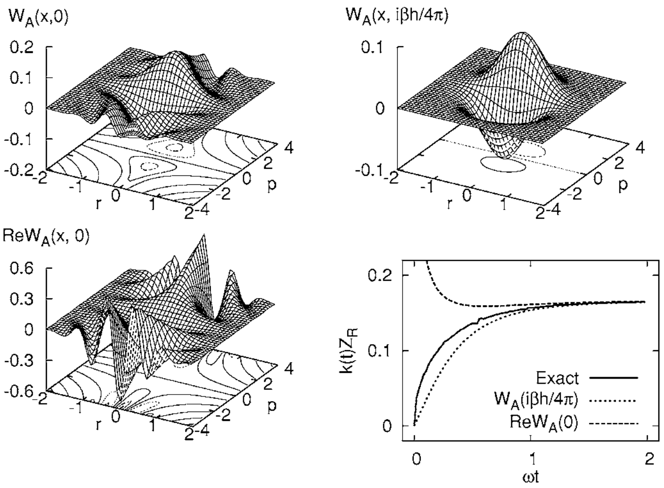

FIG. 1. Three-dimensional plots of the spectral density functions, $\bar{W}_A(x,0)$, $W_A(x,i\beta\hbar/2)$, and Re$W_A(X,0)$ in phase space. The last figure shows plots of the time dependent reaction rate coefficient $k(t)Z_R$ using each of three spectral density functions. The exact rate is obtained by numerical integration of Eq. (3). Dimensionless units are used with $\beta\hbar\omega=1$.

tion rate when the dynamics can be approximated by quantum-classical dynamics. The nonadiabatic quantum-classical version of Eq. (1) is given by[3] $k(t)n_A^{\mathrm{eq}} = \Sigma_{\alpha\alpha'}\int dX N_B^{\alpha'\alpha}(X,t)\bar{W}^{\alpha\alpha'}(X,0)$, where the nonadiabatic time evolution of $N_B^{\alpha'\alpha}(X,t)$ is given by quantum-classical Liouville dynamics.[5] As a specific example, we consider a two-level system coupled to a quartic oscillator, which is in turn bilinearly coupled to a bath of harmonic oscillators. The details of the model were described in Ref. 6.

Writing $W^{\alpha\alpha'}$ as the product of two factors, one involving the two-level system and quartic oscillator and the other the bath density conditional on the oscillator coordinate R_0, we have $W^{\alpha\alpha'}(X)=\rho_{sn}^{\alpha\alpha'}(X_0)\rho_b(X_b;R_0)$. The exact expression for $\rho_b(X_b)$ is known for the bath of harmonic oscillators.[7,8] For this system, $\bar{W}_A(X,0)$ cannot be obtained easily and $W_A(X,i\hbar\beta/2)$ provides an attractive alternative for the rate computation. From the quantum-classical version of Eq. (2) and the separation of $\hat{H}_{sn}$ into harmonic and remaining parts, we previously found an expression for $\rho_{sn}^{\alpha\alpha'}(X_0,i\hbar\beta/2)$. [See Eq. (4) in Ref. 6.]

Here, we report another useful expression

$$\rho_{sn}^{\alpha'\alpha}(X_0,0) = \frac{e^{-(2i/\hbar)P_0R_0}}{\pi\hbar M_0}\sqrt{\frac{a}{\pi}}\sum_{\alpha_1}\sqrt{\tilde{u}_1''}e^{-4aR_0^2u_1''} \times\left[\left\{P_0-\frac{i\hbar 4aR_0u_1^2}{u_1'}\right\}A_2(2R_0) - i\hbar\frac{\partial A_2(Z_0)}{\partial Z_0}\bigg|_{Z_0=2R_0}\right], \tag{4}$$

where $A_2(Z_0)=\langle\alpha';R_0|\alpha_1;R_0+Z_0/2\rangle\langle\alpha_1;-R_0+Z_0/2|\alpha;R_0\rangle$ $\exp[-\beta/2\{\varepsilon_{\alpha_1}(R_0+Z_0/2)+\varepsilon_{\alpha_1}(-R_0+Z_0/2)\}]$. The definitions of u_i and $\varepsilon_\alpha(R_0)$ are the same as those in Ref. 6. One clear advantage of Eq. (4) is that it is a closed form solution and numerical integration is not needed to obtain the result; however, initial condition sampling requires more care.

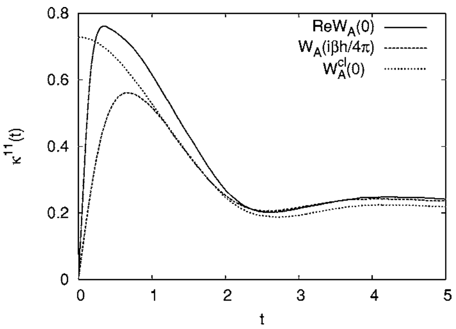

FIG. 2. Comparison of time-dependent adiabatic ground-state contributions to the transmission coefficient $\kappa^{11}(t)=k(t)/k^{\mathrm{TST}}$, where k^{TST} is the classical transition state rate constant, using three different expressions of W_A. We choose $\gamma(R_0)=\gamma_0R_0$ and the barrier frequencies $\omega_\alpha=\sqrt{-B-b_\alpha\gamma_0^2/\Omega}$. Dimensionless parameter values: $A=0.5$, $B=1$, $\gamma_0=0.1$, $\Omega=0.5$, $\beta=1$, and $\xi_K=3$.

Figure 2 clearly demonstrates that both of the quantum expressions using $W_A(X,i\hbar\beta/2)$ and Re$W_A(X,0)$ yield the same quantum rate coefficient. They serve as alternatives to the use of $\bar{W}_A(X,0)$ for the rate calculation, although they predict different transient behavior. Since the value of Re$W_A(X,0)$ is larger for larger P_0 values, an upper bound was placed on the value of Re$\rho_{sn}^{\alpha'\alpha}(0)$ to obtain more stable statistics. Since, for the system under consideration, the numerical integration involved in the computation of $W_A(X,i\hbar\beta/2)$ can be performed relatively easily and tabulated for future use, $W_A(X,i\hbar\beta/2)$ is the better choice for the rate calculation. However, for more general reaction coordinates such as the solvent polarization for proton transfer reactions,[9,10] the multidimensional integrals needed to evaluate $W_A(X,i\hbar\beta/2)$ make the computation more difficult and the simplicity of Re$W_A(X,0)$ may provide a more useful expression for the rate calculation.

To summarize, since computation of the exact Kubo-transformed quantum spectral density function $\bar{W}_A(X,0)$ is difficult for most systems, we have obtained two useful alternative expressions which yield the rate constant. The real and symmetric density function $W_A(X,i\hbar\beta/2)$ may be more suitable for simple model systems, while the simpler density function Re$W_A(X,0)$ may be more useful for complicated systems involving reaction coordinates that depend on many degrees of freedom.

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