Quantum Time-Correlation Functions

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Time correlation functions (TCFs) play essential roles in many quantum dynamical problems. For example, the generalized master equations for the reduced density dynamics of a quantum subsystem contain coefficients that are actually TCFs of the bath operators. In this page, we describe important properties of quantum time-correlation functions.

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Quantum Time Correlation Functions

A general time correlation function for general non-Hermitian operators A and B is defined as

$$C_{AB}(t) = \left[\langle A(t)B^{\dagger}(0) \rangle + \langle A^{\dagger}(t)B(0) \rangle \right] / 2,$$

where the average for canonical ensemble (thermal average) is defined as

$$\langle A(t)B^{\dagger}(0) \rangle = \mathrm{Tr}[e^{-\beta H} e^{iHt/\hbar} A e^{-iHt/\hbar} B^{\dagger}]/\mathrm{Tr}\, e^{-\beta H}.$$

More frequently we encounter autocorrelation functions for Hermitian operators:

$$C(t) = \langle A(t)A(0) \rangle.$$

Note that TCF is equilibrium properties, so we have the time-translational symmetry:

$$C(t_1, t_2) = \langle A(t_1)A(t_2) \rangle = \langle A(t_1 - t_2)A(0) \rangle = C(t_1 - t_2).$$

From the definition of TCFs, we have the following time symmetry for quantum TCFs:

$$C(-t) = C^{*}(t) = C(t - i\beta\hbar).$$

This is a very important property of the TCFs; the last expression actually manifests the detailed balance condition of the dynamics, and will guarantee correct thermal population at long times. If we define the Fourier tansform of the TCF:

$$\tilde{C}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega t} C(t)\, dt$$

Then we can obtain the detailed balance condition in Fourier space:

$$
\begin{aligned}
\tilde{C}(-\omega) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-i\omega t} C(t)\,dt \\
&= \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t} C(-t)\,dt \\
&= \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t} C(t - i\beta\hbar)\,dt \\
&= e^{-\beta\hbar\omega}\frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\omega t} C(t)\,dt \\
&= e^{-\beta\hbar\omega}\tilde{C}(\omega).
\end{aligned}
$$

Note that $C(t)$ is complex (classical TCFs are real), we can separate its real part and imaginary part,

$$
C(t) = C'(t) + iC''(t).
$$

Because $C(-t) = C^{*}(t)$, it is easy to see that

$$
\begin{aligned}
C'(t) &= C'(-t) \quad \text{(even function)}, \\
C''(t) &= -C''(-t) \quad \text{(odd function)}.
\end{aligned}
$$

Therefore

$$
\begin{aligned}
\tilde{C}(\omega) &= \frac{1}{2\pi}\int_{-\infty}^{\infty}\cos(\omega t)C'(t)\,dt - \frac{1}{2\pi}\int_{-\infty}^{\infty}\sin(\omega t)C''(t)\,dt \\
&= \tilde{C}_S(\omega) + \tilde{C}_A(\omega).
\end{aligned}
$$

$\tilde{C}(\omega)$ is a real and non-negative function of ω. It can be decompose into a symmetric (even) piece $\tilde{C}_S(\omega)$ and an anti-symmetric (odd) piece $\tilde{C}_A(\omega)$. If we consider the detailed balance condition,

$$
\tilde{C}(-\omega) = e^{-\beta\hbar\omega}\tilde{C}(\omega),
$$

we can derive the relationship between the symmetric and anti-symmetric components:

$$
\tilde{C}_A(\omega) = \tanh\!\left(\frac{\beta\hbar\omega}{2}\right)\tilde{C}_S(\omega).
$$

The above equation shows that the symmetric and asymmetric parts of the TCF in the Fourier space is related to each other. Inverse Fourier transform this and use the derivative property of the Fourier transform, we obtain the relationship between the real part and imaginary part of the TCF in time domain:

$$
C''(t) = \tan\!\left(\frac{\beta\hbar}{2}\frac{d}{dt}\right)C'(t).
$$

Note that in the classical limit $\hbar \to 0$ and the above equation gives $C''(t) = 0$, hence classical TCFs are real. In the semiclassical case $\hbar \neq 0$ and the imaginary part has to be taken into account. This equation will be our starting point for semiclassical approximations.

Harmonic Bath

Quantum time correlation function for a system coupled to a harmonic bath through a collective coordinate variable is a very useful model in quantum dynamics and spectroscopy in the condensed phase. In this case, a *spectral density* function that describes the coupling-weighted density of state for the system-bath interactions can be introduced. The derivation in the following describes the emergence of spectral density & thermal factor in the real part of the time-correlation function.

$$J(\omega) = \sum_i C_i^2 \cdot \delta(\omega - \omega_i) \Leftarrow \text{spectral density.}$$

density of states weighted by coupling strength at each mode.

must drop to both

$$H.O. \Rightarrow a(t) = a \cdot e^{-i\omega t}$$
$$a^\dagger(t) = a^\dagger \cdot e^{i\omega t}$$

$a^\dagger a$: number operator.

$$\langle a^\dagger a \rangle = \langle n \rangle = \frac{1}{e^{\beta \hbar \omega} - 1}$$

$$[a, a^\dagger] = 1$$

2nd-order TDPT $\Rightarrow \langle \hat{q}_n(t) \hat{q}_n(0) \rangle_\beta$

Assume $\hat{q} \to$ harmonic.

collective mode

$$\hat{q} \sim \hat{x}_i \Rightarrow \hat{q}_n = \sum_i C_i (a_i^\dagger + a_i)$$

coupling energy to each mode.

$$C_n(t) = \langle \hat{q}_n(t) \hat{q}_n(0) \rangle_\beta = \left\langle \sum_i C_i [a_i^\dagger(t) + a_i(t)] \cdot \sum_j C_j [a_j^\dagger + a_j] \right\rangle$$

$\Rightarrow$ if $i \neq j$, $\langle a_i^\dagger(t) a_j^\dagger \rangle = \langle a_i^\dagger(t) a_j \rangle = 0$. $\therefore$ i must $= j$

$$= \sum_{i,j} C_i C_j \cdot \left[\underbrace{\langle a_i^\dagger(t) a_j^\dagger \rangle}_{=0} + \langle a_i^\dagger(t) a_j \rangle + \langle a_i(t) a_j^\dagger \rangle + \underbrace{\langle a_i(t) a_j \rangle}_{=0} \right]$$

$$= \sum_i C_i^2 \cdot \left[\langle a_i^\dagger(t) a_i \rangle + \langle a_i(t) a_i^\dagger \rangle \right] = \sum_i C_i^2 \cdot \left[e^{i\omega t} \cdot \underbrace{\langle a_i^\dagger a_i \rangle}_{=n} + e^{-i\omega t} \cdot \underbrace{\langle a_i a_i^\dagger \rangle}_{n+1} \right]$$

$$= \sum_i C_i^2 \left[(2n+1) \cdot \cos(\omega t) - i \sin(\omega t) \right] = \int_0^\infty d\omega \left[J(\omega) \cdot \coth\left(\frac{\beta \hbar \omega}{2}\right) \cdot \cos(\omega t) - i \cdot J(\omega) \cdot \sin(\omega t) \right]$$

Calculation of quantum TCF from Molecular Dynamics

Additional Information

External Links

Research Groups

References

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