Quantum Time Correlation Function notes

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Quantum Time Correlation Functions (QTCFs) are defined as the equilibrium average over a product of hermitian operators $\hat{A}$ and $\hat{B}$,

$$C_{AB} = \langle \hat{A}(0)\hat{B}(t) \rangle$$

where the time dependent operator can be defined in the interaction picture as,

$$\hat{B}(t) = e^{i\hat{H}_0 t/\hbar}\hat{B}(0)e^{-i\hat{H}_0 t/\hbar}.$$

$\hat{H}_0$ is supposed to represent an unperturbed Hamiltonian describing our system. Time dependent systems can be easily described in the context of Perturbation Theory and this is exactly what we will discuss to show that QTCFs arise naturally when computing frequency spectra.

1 Appendix

1.1 Fourier Transform of the Symmetrized Correlation Function

In this section, we want to show how to derive the fourier transform of the symmetrized correlation function from the fourier transform of the nonsymmetrized correlation function, i.e. show that

$$\tilde{G}_{AB}(\omega) = e^{-\beta\hbar\omega/2}\tilde{C}_{AB}(\omega).$$

Equation 14.6.1 in Tuckerman's book gives the formula for the nonsymmetrized time correlation function.

$$C_{AB}(t) = \frac{1}{Q}\text{Tr}\left[e^{-\beta H}\hat{A}e^{iHt/\hbar}\hat{B}e^{-iHt/\hbar}\right]$$

The trace can be evaluated in the energy basis as,

$$C_{AB}(t) = \frac{1}{Q}\sum_n \langle E_n | e^{-\beta H}\hat{A}e^{iHt/\hbar}\hat{B}e^{-iHt/\hbar} | E_n \rangle.$$

Then the resolution of identity can be inserted between A and B.

$$C_{AB}(t) = \frac{1}{Q}\sum_n \sum_m \langle E_n | e^{-\beta H}\hat{A}e^{iHt/\hbar} | E_m \rangle \langle E_m | \hat{B}e^{-iHt/\hbar} | E_n \rangle$$

$$= \frac{1}{Q}\sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle e^{-\beta E_n}e^{iE_m t/\hbar}e^{-iE_n t/\hbar}$$

$$= \frac{1}{Q}\sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle e^{-\beta E_n}e^{i(E_m - E_n)t/\hbar}$$

Taking the fourier transform of $C_{AB}(t)$ gives a function in terms of ω, $\tilde{C}_{AB}(\omega)$.

$$
\begin{aligned}
\tilde{C}_{AB}(\omega) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-i\omega t} C_{AB}(t) dt \\
&= \frac{1}{Q} \sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle e^{-\beta E_n} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-i\omega t} e^{i(E_m - E_n)t/\hbar} dt \\
&= \frac{1}{Q} \sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle e^{-\beta E_n} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{i(E_m - E_n - \hbar\omega)t/\hbar} dt \\
&= \frac{1}{Q} \sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle e^{-\beta E_n} \frac{1}{\sqrt{2\pi}} \left[2\pi\hbar\delta(E_m - E_n - \hbar\omega) \right] \\
&= \frac{1}{Q} \sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle e^{-\beta E_n} \sqrt{2\pi}\hbar\delta(E_m - E_n - \hbar\omega)
\end{aligned}
$$

We can do the exact same procedure to find the fourier transform of the symmetrized time correlation function $\tilde{G}_{AB}$. Equation 14.6.4 gives us our starting point,

$$
G_{AB}(t) = \frac{1}{Q} \text{Tr}[\hat{A} e^{iH\tau^*/\hbar} \hat{B} e^{-iH\tau/\hbar}]
$$

where τ is a complex time variable $\tau = t - i\beta\hbar/2$. Now we evaluate $G_{AB}(t)$ in the energy basis.

$$
\begin{aligned}
G_{AB}(t) &= \frac{1}{Q} \sum_n \langle E_n | \hat{A} e^{iH\tau^*/\hbar} \hat{B} e^{-iH\tau/\hbar} | E_n \rangle \\
&= \frac{1}{Q} \sum_n \sum_m \langle E_n | \hat{A} e^{iH\tau^*/\hbar} | E_m \rangle \langle E_m | \hat{B} e^{-iH\tau/\hbar} | E_n \rangle \\
&= \frac{1}{Q} \sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle e^{iE_m\tau^*/\hbar} e^{-iE_n\tau/\hbar} \\
&= \frac{1}{Q} \sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle e^{iE_m(t+i\beta\hbar/2)/\hbar} e^{-iE_n(t-i\beta\hbar/2)/\hbar} \\
&= \frac{1}{Q} \sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle e^{-\beta E_m/2} e^{-\beta E_n/2} e^{i(E_m - E_n)t/\hbar}
\end{aligned}
$$

Performing a fourier transform gives us,

$$
\begin{aligned}
\tilde{G}_{AB}(\omega) &= \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-i\omega t} G_{AB}(t) dt \\
&= \frac{1}{Q} \sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle e^{-\beta E_m/2} e^{-\beta E_n/2} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-i\omega t} e^{i(E_m - E_n)t/\hbar} dt \\
&= \frac{1}{Q} \sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle e^{-\beta E_m/2} e^{-\beta E_n/2} \sqrt{2\pi}\hbar\delta(E_m - E_n - \hbar\omega)
\end{aligned}
$$

If we mutliply $\tilde{G}_{AB}(\omega)$ with $e^{\beta\hbar\omega/2}$, we can make use of the fact that the delta function will make every term in the sums zero except for the ones where $E_m - E_n = \hbar\omega$. This gives us the relationship $E_m = E_n + \hbar\omega$, which we can now

plug in to get,

$$e^{\beta\hbar\omega/2}\tilde{G}_{AB}(\omega) = \frac{1}{Q}\sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle \, e^{\beta\hbar\omega/2} e^{-\beta E_m/2} e^{-\beta E_n/2} \sqrt{2\pi}\hbar\delta(E_m - E_n - \hbar\omega)$$

$$= \frac{1}{Q}\sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle \, e^{\beta\hbar\omega/2} e^{-\beta(E_n + \hbar\omega)/2} e^{-\beta E_n/2} \sqrt{2\pi}\hbar\delta(E_m - E_n - \hbar\omega)$$

$$= \frac{1}{Q}\sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle \, e^{(\beta\hbar\omega - \beta E_n - \beta\hbar\omega - \beta E_n)/2} \sqrt{2\pi}\hbar\delta(E_m - E_n - \hbar\omega)$$

$$= \frac{1}{Q}\sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle \, e^{(-2\beta E_n)/2} \sqrt{2\pi}\hbar\delta(E_m - E_n - \hbar\omega)$$

$$= \frac{1}{Q}\sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle \, e^{-\beta E_n} \sqrt{2\pi}\hbar\delta(E_m - E_n - \hbar\omega)$$

$$= \tilde{C}_{AB}(\omega).$$

1.2 Fourier Transform of the Kubo-Transformed Correlation Function

In this section, we want to show how to derive the fourier transform of the nonsymmetrized correlation function from the fourier transform of the kubo-transformed correlation function, i.e. show that

$$\tilde{C}_{AB}(\omega) = \left[\frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}}\right]\tilde{K}_{AB}(\omega)$$

We start with the definition of the kubo-transformed correlation function,

$$K_{AB}(t) = \frac{1}{\beta Q}\int_0^\beta d\lambda \, \mathrm{Tr}\left[e^{-(\beta - \lambda)H}\hat{A}e^{-\lambda H}e^{iHt/\hbar}\hat{B}e^{-iHt/\hbar}\right]$$

Just as we did in the previous section, we start by finding $K_{AB}(t)$ in the energy basis.

$$K_{AB}(t) = \frac{1}{\beta Q}\int_0^\beta d\lambda \, \mathrm{Tr}\left[e^{-(\beta - \lambda)H}\hat{A}e^{-\lambda H}e^{iHt/\hbar}\hat{B}e^{-iHt/\hbar}\right]$$

$$= \frac{1}{\beta Q}\int_0^\beta d\lambda \, \sum_n \langle E_n | e^{-(\beta - \lambda)H}\hat{A}e^{-\lambda H}e^{iHt/\hbar}\hat{B}e^{-iHt/\hbar} | E_n \rangle$$

$$= \frac{1}{\beta Q}\int_0^\beta d\lambda \, \sum_n \sum_m \langle E_n | e^{-(\beta - \lambda)H}\hat{A}e^{-\lambda H}e^{iHt/\hbar} | E_m \rangle \langle E_m | \hat{B}e^{-iHt/\hbar} | E_n \rangle$$

$$= \frac{1}{\beta Q}\int_0^\beta d\lambda \, \sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle \, e^{-(\beta - \lambda)E_n}e^{-\lambda E_m}e^{iE_m t/\hbar}e^{-iE_n t/\hbar}$$

$$= \frac{1}{\beta Q}\int_0^\beta d\lambda \, \sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle \, e^{-(\beta - \lambda)E_n}e^{-\lambda E_m}e^{i(E_m - E_n)t/\hbar}$$

We can interchange the integral and the sum since they are both independent of each other,

$$K_{AB}(t) = \frac{1}{\beta Q}\sum_n \sum_m \langle E_n | \hat{A} | E_m \rangle \langle E_m | \hat{B} | E_n \rangle \, e^{i(E_m - E_n)t/\hbar}\int_0^\beta e^{-(\beta - \lambda)E_n}e^{-\lambda E_m}d\lambda$$

and evaluate the simple integral.

$$\int_0^\beta e^{-(\beta - \lambda)E_n}e^{-\lambda E_m}d\lambda = e^{-\beta E_n}\int_0^\beta e^{\lambda(E_n - E_m)}d\lambda$$

$$= \frac{e^{-\beta E_n}}{E_n - E_m}e^{\lambda(E_n - E_m)}\Big|_0^\beta$$

$$= \frac{e^{-\beta E_n}}{E_n - E_m}\left[e^{\beta(E_n - E_m)} - 1\right]$$

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So our correlation function becomes,

$$K_{AB}(t) = \frac{1}{\beta Q} \sum_n \sum_m \langle E_n| \hat{A} |E_m\rangle \langle E_m| \hat{B} |E_n\rangle e^{i(E_m - E_n)t/\hbar} \frac{e^{-\beta E_n}}{E_n - E_m}\left[e^{\beta(E_n - E_m)} - 1\right]$$

And now we find $\tilde{K}_{AB}$ with the fourier transform,

$$\tilde{K}_{AB}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-i\omega t} K_{AB}(t)$$

$$= \frac{1}{\beta Q} \sum_n \sum_m \langle E_n| \hat{A} |E_m\rangle \langle E_m| \hat{B} |E_n\rangle \frac{e^{-\beta E_n}}{E_n - E_m}\left[e^{\beta(E_n - E_m)} - 1\right] \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} e^{-i\omega t} e^{i(E_m - E_n)t/\hbar} dt$$

$$= \frac{1}{\beta Q} \sum_n \sum_m \langle E_n| \hat{A} |E_m\rangle \langle E_m| \hat{B} |E_n\rangle \frac{e^{-\beta E_n}}{E_n - E_m}\left[e^{\beta(E_n - E_m)} - 1\right] \sqrt{2\pi}\hbar\delta(E_m - E_n - \hbar\omega)$$

Then we mutliply $\tilde{K}_{AB}$ by the factor of interest,

$$\left[\frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}}\right]\tilde{K}_{AB}(\omega) = \frac{1}{\beta Q} \sum_n \sum_m \langle E_n| \hat{A} |E_m\rangle \langle E_m| \hat{B} |E_n\rangle \left(\frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}}\right)\left(\frac{e^{-\beta E_n}}{E_n - E_m}\right)\left(e^{\beta(E_n - E_m)} - 1\right)\sqrt{2\pi}\hbar\delta(E_m - E_n - \hbar\omega)$$

and use the fact that the only nonzero terms in the sums are the ones where $E_m = E_n + \hbar\omega$ to replace E_m. So the multiplication of all 3 terms in paranthesis becomes,

$$\left(\frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}}\right)\left(\frac{e^{-\beta E_n}}{E_n - E_m}\right)\left(e^{\lambda(E_n - E_m)} - 1\right) = \left(\frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}}\right)\left(\frac{e^{-\beta E_n}}{E_n - (E_n + \hbar\omega)}\right)\left(e^{\beta(E_n - (E_n + \hbar\omega))} - 1\right)$$

$$= \left(\frac{-\beta e^{-\beta E_n}}{1 - e^{-\beta\hbar\omega}}\right)\left(e^{-\beta\hbar\omega} - 1\right)$$

$$= \beta e^{-\beta E_n}.$$

This gives us,

$$\left[\frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}}\right]\tilde{K}_{AB}(\omega) = \frac{1}{\beta Q} \sum_n \sum_m \langle E_n| \hat{A} |E_m\rangle \langle E_m| \hat{B} |E_n\rangle \beta e^{-\beta E_n} \sqrt{2\pi}\hbar\delta(E_m - E_n - \hbar\omega)$$

$$= \frac{1}{Q} \sum_n \sum_m \langle E_n| \hat{A} |E_m\rangle \langle E_m| \hat{B} |E_n\rangle e^{-\beta E_n} \sqrt{2\pi}\hbar\delta(E_m - E_n - \hbar\omega)$$

$$= \tilde{C}_{AB}(\omega).$$