5.2. QUANTUM CORRELATION FUNCTIONS

Quantum correlation functions involve the equilibrium (thermal) average over a product of Hermitian operators evaluated two times. The thermal average is implicit in writing $C_{AA}(t,t') = \langle A(t)A(t') \rangle$. Naturally, this also invokes a Heisenberg representation of the operators, although in almost all cases, we will be writing correlation functions as interaction picture operators $A_i(t) = e^{iH_0 t} A e^{-iH_0 t}$.

To emphasize the thermal average, the quantum correlation function can also be written as

$$C_{AA}(t,t') = \left( \frac{e^{-\beta H}}{Z} A(t)A(t') \right)$$

If we evaluate this in a basis set $|n\rangle$, inserting a projection operator leads to our previous expression

$$C_{AA}(t,t') = \sum_n p_n \langle n | A(t)A(t') | n \rangle$$

with $p_n = e^{-\beta E_n}/Z$. Given the case of a time-independent Hamiltonian, we can also express this in the Schrödinger picture

$$C_{AA}(t,t') = \sum_n p_n \langle n | U^\dagger(t)AU(t)U^\dagger(t')AU(t')A | n \rangle$$

$$= \sum_n p_n \langle n |AU(t-t')A | n \rangle e^{i\omega_n(t-t')}$$

$$= \sum_{n,m} p_n \langle n | A | m \rangle \langle m | A | n \rangle e^{-i\omega_m(t-t')}$$

$$= \sum_{n,m} p_n |A_{mn}|^2 e^{-i\omega_m(t-t')}$$

Properties of Quantum Correlation Functions

There are a few properties of quantum correlation functions that can be obtained using the properties of the time-evolution operator. First, we can show the property of stationarity, which we have come to expect:
\[ \langle A(t)A(t') \rangle = \langle U(t')A(0)U(t)U(t')A(0)U(t') \rangle = \langle U(t')U(t')AU(t)U(t')A \rangle = \langle A(t-t')A(0) \rangle \] (5.38)

Also, we can show that
\[ \langle A(-t)A(0) \rangle = \langle A(t)A(0) \rangle^* = \langle A(0)A(t) \rangle \] (5.39)

or
\[ C_{AA}^* (t) = C_{AA} (-t) \] (5.40)

This follows from
\[ \langle A(0)A(t) \rangle = \langle A(0)U^* AU \rangle = \langle U^* AU \rangle = \langle A(-t)A(0) \rangle \] (5.41)

\[ \langle A(t)A(0) \rangle^* = \langle U^* AU \rangle = \langle U^* AU \rangle = \langle A(0)A(t) \rangle \] (5.42)

Note that the quantum \( C_{AA} (t) \) is complex. You cannot directly measure a quantum correlation function, but observables are often related to the real or imaginary part of correlation functions, or other combinations of correlation functions.

\[ C_{AA}(t) = C_{AA}^*(t) + i C_{AA}^*(t) \] (5.43)

\[ C_{AA}'(t) = \frac{1}{2} [ C_{AA}(t) + C_{AA}^*(t) ] = \frac{1}{2} [ \langle A(t)A(0) \rangle + \langle A(0)A(t) \rangle ] \] (5.44)

\[ C_{AA}''(t) = \frac{1}{2i} [ C_{AA}(t) - C_{AA}^*(t) ] = \frac{1}{2i} [ \langle A(t)A(0) \rangle - \langle A(0)A(t) \rangle ] \] (5.45)

We will see later in our discussion of linear response that \( C_{AA}' \) and \( C_{AA}'' \) are directly proportional to the step response function \( S \) and the impulse response function \( R \), respectively. \( R \) describes how a system is driven away from equilibrium by an external potential, whereas \( S \) describes the relaxation of the system to equilibrium when a force holding it away from equilibrium is released. The two are related by \( R \propto \partial S/\partial t \).
We can also define a spectral or frequency-domain correlation function by Fourier transforming the TCF.

\[ \tilde{C}_{AA}(\omega) = \tilde{F}\left[ C_{AA}(t) \right] = \int_{-\infty}^{\infty} dt e^{i\omega t} C_{AA}(t) \] (5.46)

For a time-independent Hamiltonian, as we might have in an interaction picture problem, the TCF in eq. (5.37) gives

\[ \tilde{C}_{AA}(\omega) = \sum_{n,m} p_n |A_{mn}|^2 \delta(\omega - \omega_{nm}). \] (5.47)

This expression looks very similar to the Golden rule transition rate from first order perturbation theory. In fact, the Fourier transform of time correlation functions evaluated at the energy gap gives the transition rate between states that we obtain from 1st order perturbation theory. Note that this expression is valid whether the initial states \( n \) are higher or lower in energy than final states \( m \), and accounts for upward and downward transitions. If we compare the ratio of upward and downward transition rates between two states \( i \) and \( j \), we have

\[ \frac{\tilde{C}_{AA}(\omega_j)}{\tilde{C}_{AA}(\omega_i)} = \frac{p_j}{p_i} = e^{\beta E_{ij}}. \] (5.48)

This is one way of showing the principle of detailed balance, which relates upward and downward transition rates at equilibrium to the difference in thermal occupation between states:

\[ \tilde{C}_{AA}(\omega) = e^{\beta \hbar \omega} \tilde{C}_{AA}(-\omega). \] (5.49)