

III.1.3 Non-symmetrized and symmetrized correlation functions

In this section and the next two ones, we consider generic operators \hat{A} and \hat{B} , which might not necessarily be Hermitian unless we specify it.

In the equilibrium state $\hat{\rho}_{\text{eq}}$, the *non-symmetrized correlation function* between the operators \hat{A} and \hat{B} at different times t, t' is defined as

$$C_{BA}(t, t') \equiv \langle \hat{B}_I(t) \hat{A}_I(t') \rangle_{\text{eq}}. \quad (\text{III.11})$$

Due the stationarity of the equilibrium state, the expectation value on the right-hand side is invariant under time translations, so that $C_{BA}(t, t') = C_{BA}(t - t', 0)$.

Mathematically, the latter identity is easily checked by inserting explicitly the terms $e^{\pm i\hat{H}_0 t/\hbar}$, $e^{\pm i\hat{H}_0 t'/\hbar}$ in definition (III.11) and by using the invariance of the trace under cyclic permutations and the commutativity of $\hat{\rho}_{\text{eq}}$ and \hat{H}_0 .

One may thus replace the two variables by their difference $\tau \equiv t - t'$ and define equivalently

$$C_{BA}(\tau) \equiv \langle \hat{B}_I(\tau) \hat{A} \rangle_{\text{eq}}, \quad (\text{III.12})$$

where we used $\hat{A}_I(0) = \hat{A}$ (41)

Introducing the representation of the operators in the basis of the energy eigenstates, a straightforward calculation gives the alternative form

$$C_{BA}(\tau) = \sum_{n, n'} \pi_n B_{nn'} A_{n'n} e^{-i\omega_{n'n}\tau}. \quad (\text{III.13})$$

This leads at once to the Fourier transform

$$\tilde{C}_{BA}(\omega) \equiv \int_{-\infty}^{\infty} C_{BA}(\tau) e^{i\omega\tau} d\tau = 2\pi \sum_{n, n'} \pi_n B_{nn'} A_{n'n} \delta(\omega - \omega_{n'n}). \quad (\text{III.14})$$

This expression shows the generic property of the dependence of correlation functions on the excitations frequencies of the system. More precisely, $\tilde{C}_{BA}(\omega)$ clearly diverges when the angular frequency ω coincides with one of the Bohr frequencies of the system, unless the associated matrix element of \hat{A} or \hat{B} vanishes—for instance, because the corresponding transition between energy eigenstates is forbidden by some selection rule.

Even if \hat{A} and \hat{B} are Hermitian, the correlation function (III.12) is generally not real-valued: with the cyclicity of the trace, one finds

$$C_{BA}(\tau)^* = \langle \hat{B}_I(\tau) \hat{A} \rangle_{\text{eq}}^* = \langle \hat{A}^\dagger \hat{B}_I^\dagger(\tau) \rangle_{\text{eq}} = C_{A^\dagger B^\dagger}(-\tau), \quad (\text{III.15})$$

which has in general no obvious relation to $C_{BA}(\tau)$.

⁽⁴³⁾Strictly speaking, the condition $f(t) \rightarrow 0$ as $t \rightarrow -\infty$ does not hold here, yet one can easily branch the sinusoidal perturbation adiabatically—mathematically with a factor $e^{\epsilon t}$ for $-\infty < t \leq 0$ with $\epsilon \rightarrow 0^+$ —and recover the same result for $t > 0$.

To characterize the correlations between observables \hat{A} and \hat{B} by a real-valued quantity, one introduces the *symmetric correlation function*

$$S_{BA}(\tau) \equiv \frac{1}{2} \left\langle \{ \hat{B}_I(\tau), \hat{A} \}_+ \right\rangle_{\text{eq.}}, \quad (\text{III.16})$$

where $\{ \cdot, \cdot \}_+$ denotes the anticommutator of two operators. Using definition (III.12), one finds at once

$$S_{BA}(\tau) = \frac{1}{2} [C_{BA}(\tau) + C_{AB}(-\tau)]. \quad (\text{III.17})$$

In the case of observables, the associated operators are Hermitian, $\hat{A} = \hat{A}^\dagger$ and $\hat{B} = \hat{B}^\dagger$, so that relation (III.15) reads $C_{AB}(-\tau) = C_{BA}(\tau)^*$, which implies that $S_{BA}(\tau)$ is a real number.

The representation (III.13) of the non-symmetrized correlation function gives

$$C_{AB}(-\tau) = \sum_{n,n'} \pi_n A_{nn'} B_{n'n} e^{i\omega_{n'n}\tau} = \sum_{n,n'} \pi_n A_{nn'} B_{n'n} e^{-i\omega_{nn'}\tau} = \sum_{n,n'} \pi_{n'} A_{n'n} B_{nn'} e^{-i\omega_{n'n}\tau},$$

where the second identity comes from the obvious identity $\omega_{nn'} = -\omega_{n'n}$, while the last one follows from exchanging the dummy indices n, n' . Taking the half sum of this decomposition and Eq. (III.13) and Fourier transforming, one finds

$$\tilde{S}_{BA}(\omega) = \pi \sum_{n,n'} (\pi_n + \pi_{n'}) B_{nn'} A_{n'n} \delta(\omega - \omega_{n'n}). \quad (\text{III.18})$$

III.1.4 Spectral density

Instead of considering (half) the expectation value of the anticommutator of $\hat{B}_I(\tau)$ and \hat{A} , one can also think of introducing that of the commutator. Inserting a factor $1/\hbar$ to ensure a proper behavior in the classical limit, we thus define

$$\xi_{BA}(\tau) \equiv \frac{1}{2\hbar} \left\langle [\hat{B}_I(\tau), \hat{A}] \right\rangle_{\text{eq.}}. \quad (\text{III.19})$$

Repeating identically the steps leading from the definition (III.16) of the symmetrized correlation function to its Fourier transform (III.18), one finds the so-called *spectral function* (or *spectral density*)

$$\tilde{\xi}_{BA}(\omega) \equiv \frac{\pi}{\hbar} \sum_{n,n'} (\pi_n - \pi_{n'}) B_{nn'} A_{n'n} \delta(\omega - \omega_{n'n}), \quad (\text{III.20})$$

with as usual $\omega_{n'n}$ the Bohr frequencies of the system, and $A_{nn'}$, $B_{nn'}$ the matrix elements of the operators \hat{A} , \hat{B} between energy eigenstates.

The spectral density is in general complex-valued, yet becomes real-valued when one considers the autocorrelation of an observable, i.e. for $\hat{B} = \hat{A}^\dagger = \hat{A}$, in which case $B_{nn'} A_{n'n} = |A_{n'n}|^2$.

III.1.5 Canonical correlation function

Last we introduce Kubo's *canonical correlation function*, defined as [33]

$$K_{BA}(\tau) \equiv \frac{1}{\beta} \int_0^\beta \left\langle e^{\lambda \hat{H}_0} \hat{A} e^{-\lambda \hat{H}_0} \hat{B}_I(\tau) \right\rangle_{\text{eq.}} d\lambda = \frac{1}{\beta} \int_0^\beta \left\langle \hat{A}_I(-i\hbar\lambda) \hat{B}_I(\tau) \right\rangle_{\text{eq.}} d\lambda, \quad (\text{III.21})$$

for a system governed by the Hamilton operator \hat{H}_0 , where β is the inverse temperature of the equilibrium state.

Using the explicit form of the equilibrium distribution $\hat{\rho}_{\text{eq}}$ —or equivalently, of the populations π_n of the energy eigenstates at canonical equilibrium—, one finds the Fourier transform

$$\tilde{K}_{BA}(\omega) \equiv \int_{-\infty}^{\infty} K_{BA}(\tau) e^{i\omega\tau} d\tau = 2\pi \sum_{n,n'} \frac{\pi_n - \pi_{n'}}{\beta\hbar\omega_{n'n}} B_{nn'} A_{n'n} \delta(\omega - \omega_{n'n}). \quad (\text{III.22})$$

Proof of the spectral decomposition (III.22):

The equilibrium expectation value in the integrand of definition (III.21) reads

$$\sum_{n,n'} \pi_{n'} e^{\lambda E_{n'}} A_{n'n} e^{-\lambda E_n} B_{nn'} e^{i\omega_{nn'}\tau} = \sum_{n,n'} \pi_{n'} e^{\lambda\hbar\omega_{n'n}} B_{nn'} A_{n'n} e^{-i\omega_{n'n}\tau}.$$

The integration over λ is straightforward and gives

$$K_{BA}(\tau) = \frac{1}{\beta} \sum_{n,n'} \frac{e^{\beta\hbar\omega_{n'n}} - 1}{\hbar\omega_{n'n}} \pi_{n'} B_{nn'} A_{n'n} e^{-i\omega_{n'n}\tau} = \sum_{n,n'} \frac{\pi_n - \pi_{n'}}{\beta\hbar\omega_{n'n}} B_{nn'} A_{n'n} e^{-i\omega_{n'n}\tau}, \quad (\text{III.23})$$

where the second identity comes from $e^{\beta\hbar\omega_{n'n}} = \pi_n/\pi_{n'}$, which follows from Eq. (III.2b). This alternative representation of the Kubo correlation function leads at once to the Fourier transform (III.22).

III.2 Physical meaning of the correlation functions

In the previous Section, we left a few issues open. First we defined the linear response function by introducing its role in a given physical situation, but did not attempt to compute it, which will now be done perturbatively in § III.2.1. Adopting then a somewhat opposite approach, we introduced several correlation functions mathematically, without discussing the physical phenomena they embody. Again, we shall remedy this now, in § III.2.2–III.2.4.

III.2.2 Dissipation

Consider a system subject to a harmonic perturbation $\hat{W} \cos \omega t$ with constant \hat{W} . A straightforward application of time-dependent perturbation theory in quantum mechanics yields for the transition rate from an arbitrary initial state $|\phi_i\rangle$ to the set of corresponding final states $|\phi_f\rangle$

$$\Gamma_{i \rightarrow f} = \frac{\pi}{2\hbar^2} \sum_f |\langle \phi_f | \hat{W} | \phi_i \rangle|^2 [\delta(\omega_{fi} - \omega) + \delta(\omega_{if} - \omega)]. \quad (\text{III.30})$$

If the system absorbs energy from the perturbation, then $E_f > E_i$, so that only the first δ -term contributes. On the other hand, energy release from the system, corresponding to “induced emission”, requires $E_f < E_i$, i.e. involves the second δ -term.

We apply this result to the system of § III.1.1, initially at thermodynamic equilibrium. Let $f(t) = f_\omega \cos \omega t$, with constant real f_ω , be a “force” coupling to an operator \hat{A} acting on the system, leading to the perturbation (III.7) in the Hamiltonian.

The probability per unit time that the system absorb a quantum $\hbar\omega$ of energy starting from an initial state $|\phi_n\rangle$ is given by Eq. (III.30) with $|\phi_i\rangle = |\phi_n\rangle$ and keeping only the first δ -term. Multiplying this probability by the initial state population π_n and by the absorbed energy $\hbar\omega$, and summing over all possible initial states, one finds the total energy received per unit time by the system

$$\mathcal{P}_{\text{gain}} = \frac{\pi f_\omega^2}{2\hbar^2} \sum_{n,n'} \pi_n \hbar\omega |A_{nn'}|^2 \delta(\omega_{n'n} - \omega).$$

An analogous reasoning gives for the total energy emitted by the system per unit time

$$-\mathcal{P}_{\text{loss}} = \frac{\pi f_\omega^2}{2\hbar^2} \sum_{n,n'} \pi_n \hbar\omega |A_{nn'}|^2 \delta(\omega_{nn'} - \omega) = \frac{\pi f_\omega^2}{2\hbar^2} \sum_{n,n'} \pi_{n'} \hbar\omega |A_{nn'}|^2 \delta(\omega_{n'n} - \omega),$$

where in the second identity we have exchanged the roles of the two dummy indices. Note that since the system is at thermodynamic equilibrium, the lower energy levels are more populated, so that the absorption term is larger than the emission term.

Adding $\mathcal{P}_{\text{gain}}$ and $\mathcal{P}_{\text{loss}}$ yields the net total energy exchanged—and actually absorbed by the system—per unit time, dE_{tot}/dt , when it is submitted to a perturbation $-f_\omega \hat{A} \cos \omega t$, namely

$$\frac{dE_{\text{tot}}}{dt} = \frac{\pi f_\omega^2 \omega}{2\hbar} \sum_{n,n'} (\pi_n - \pi_{n'}) |A_{nn'}|^2 \delta(\omega_{n'n} - \omega).$$

Under consideration of the definition (III.20) of the spectral density, this also reads

$$\frac{dE_{\text{tot}}}{dt} = \frac{f_\omega^2}{2} \omega \tilde{\xi}_{A^\dagger A}(\omega). \quad (\text{III.31})$$

The spectral function $\tilde{\xi}_{A^\dagger A}(\omega)$ thus characterizes the dissipation of energy in the system when it is submitted to a small perturbation proportional to $\hat{A} \cos \omega t$.

III.2.3 Relaxation

Let us now assume that the external “force” at equilibrium in the excitation (III.7) acting on the system of § III.1.1 is given by

$$f(t) = f e^{\varepsilon t} \Theta(-t), \quad (\text{III.32})$$

with a constant f , where at the end of calculations we shall take the limit $\varepsilon \rightarrow 0^+$. This force represents a perturbation turned on from $t = -\infty$ over the typical scale ε^{-1} , slowly driving the system out of its initial equilibrium state. At $t = 0$, the perturbation is turned off, and the system then relaxes to the original equilibrium state. We shall now compute the departure from equilibrium of the expectation value of an operator \hat{B} due to this excitation.

Inserting Eq. (III.32) in the Kubo formula (III.8), one finds

$$\begin{aligned} \frac{1}{f} \left[\langle \hat{B}_I(t) \rangle_{\text{n.eq.}} - \langle \hat{B} \rangle_{\text{eq.}} \right] &= \int_{-\infty}^{\infty} \chi_{BA}(t-t') e^{\varepsilon t'} \Theta(-t') dt' \\ &= \int_{-\infty}^{\infty} e^{\varepsilon t'} \Theta(-t') \int_{-\infty}^{\infty} \tilde{\chi}_{BA}(\omega) e^{-i\omega(t-t')} \frac{d\omega}{2\pi} dt', \end{aligned}$$

where we have introduced the generalized susceptibility. Exchanging the order of the integrals and performing that over t' give

$$\frac{1}{f} \left[\langle \hat{B}_I(t) \rangle_{\text{n.eq.}} - \langle \hat{B} \rangle_{\text{eq.}} \right] = \int_{-\infty}^{\infty} \frac{\tilde{\chi}_{BA}(\omega)}{i\omega + \varepsilon} e^{-i\omega t} \frac{d\omega}{2\pi}.$$

That is, the linear response $\langle \hat{B}_I(t) \rangle_{\text{n.eq.}} - \langle \hat{B} \rangle_{\text{eq.}}$ is proportional to the inverse Fourier transform of the ratio of the generalized susceptibility over $i\omega + \varepsilon = i(\omega - i\varepsilon)$.

Expressing $\tilde{\chi}_{BA}(\omega)$ in terms of the spectral function with Eq. (III.29) and exchanging the order of the integrals, the above relation becomes

$$\frac{1}{f} \left[\langle \hat{B}_I(t) \rangle_{\text{n.eq.}} - \langle \hat{B} \rangle_{\text{eq.}} \right] = \frac{1}{\pi} \lim_{\varepsilon' \rightarrow 0^+} \int_{-\infty}^{\infty} \tilde{\xi}_{BA}(\omega') \left[\int_{-\infty}^{\infty} \frac{e^{-i\omega t}}{(\omega - i\varepsilon)(\omega' - \omega - i\varepsilon')} \frac{d\omega}{2\pi i} \right] d\omega'. \quad (\text{III.33})$$

The integration over ω is then straightforward with the theorem of residues, where the term $e^{-i\omega t}$ dictates whether the integration contour consisting of the real axis and a half-circle at infinity should be closed in the upper (for $t < 0$) or in the lower (for $t > 0$) complex half-plane of the variable ω .

- For $t < 0$, one has to consider the only pole of the integrand in the upper half-plane, which lies at $\omega = i\varepsilon$. The corresponding residue is $e^{\varepsilon t}/(\omega' - i\varepsilon - i\varepsilon')$, which yields

$$\langle \hat{B}_I(t) \rangle_{\text{n.eq.}} - \langle \hat{B} \rangle_{\text{eq.}} = \frac{f e^{\varepsilon t}}{\pi} \lim_{\varepsilon' \rightarrow 0^+} \int_{-\infty}^{\infty} \frac{\tilde{\xi}_{BA}(\omega')}{\omega' - i\varepsilon - i\varepsilon'} d\omega' = \frac{f(t)}{\pi} \int_{-\infty}^{\infty} \frac{\tilde{\xi}_{BA}(\omega')}{\omega' - i\varepsilon} d\omega'.$$

Taking now the limit $\varepsilon \rightarrow 0^+$ and using relation (III.29) for $\omega = 0$, one obtains

$$\langle \hat{B}_I(t) \rangle_{\text{n.eq.}} - \langle \hat{B} \rangle_{\text{eq.}} = f(t) \tilde{\chi}_{BA}(0) \quad \text{for } t \leq 0. \quad (\text{III.34})$$

This result is easily interpreted: the system is driven out of equilibrium so slowly that the departure of the expectation value of $\hat{B}_I(t)$ from the equilibrium value can be computed with the help of the *static* susceptibility, i.e. $\tilde{\chi}_{BA}(0)$ at zero frequency.

- For $t > 0$, the only pole in the lower half-plane of the integrand in Eq. (III.33) is at $\omega = \omega' - i\varepsilon'$. This leads to

$$\begin{aligned} \frac{1}{f} \left[\langle \hat{B}_I(t) \rangle_{\text{n.eq.}} - \langle \hat{B} \rangle_{\text{eq.}} \right] &= \frac{1}{\pi} \lim_{\varepsilon' \rightarrow 0^+} \int_{-\infty}^{\infty} \frac{\tilde{\xi}_{BA}(\omega')}{\omega' - i\varepsilon - i\varepsilon'} e^{-i(\omega' - i\varepsilon')t} d\omega' \quad \text{for } t > 0 \quad (\text{III.35}) \\ &= \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\tilde{\xi}_{BA}(\omega')}{\omega' - i\varepsilon} e^{-i\omega' t} d\omega'. \end{aligned}$$

Replacing the spectral density by its explicit expression (III.20) and exchanging the sum and the integral, one finds

$$\begin{aligned} \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\tilde{\xi}_{BA}(\omega')}{\omega' - i\varepsilon} e^{-i\omega' t} d\omega' &= \frac{1}{\hbar} \sum_{n,n'} (\pi_n - \pi_{n'}) B_{nm'} A_{n'n} \int_{-\infty}^{\infty} \frac{e^{-i\omega' t}}{\omega' - i\varepsilon} \delta(\omega - \omega_{n'n}) d\omega' \\ &= \frac{1}{\hbar} \sum_{n,n'} (\pi_n - \pi_{n'}) B_{nm'} A_{n'n} \frac{e^{-i\omega_{n'n} t}}{\omega_{n'n} - i\varepsilon}. \end{aligned}$$

In the limit $\varepsilon \rightarrow 0^+$, one recognizes on the right-hand side the spectral decomposition (III.23) of the canonical correlation function

$$\frac{1}{\pi} \lim_{\varepsilon \rightarrow 0^+} \int_{-\infty}^{\infty} \frac{\tilde{\xi}_{BA}(\omega)}{\omega - i\varepsilon} e^{-i\omega t} d\omega = \beta K_{BA}(t). \quad (\text{III.36})$$

Inserting this identity in the above expression of the departure from equilibrium of the average value of $\hat{B}_I(t)$ finally gives

$$\frac{1}{f} \left[\langle \hat{B}_I(t) \rangle_{\text{n.eq.}} - \langle \hat{B} \rangle_{\text{eq.}} \right] = \beta K_{BA}(t) \quad \text{for } t > 0. \quad (\text{III.37})$$

That is, the Kubo correlation function describes the relaxation from an out-of-equilibrium state—which justifies why Kubo called it⁽⁴⁴⁾ “relaxation function” in his original paper^[33].

Remark: Instead of letting ε' go to 0^+ in Eq. (III.35), one may as well take first the (trivial) limit $\varepsilon \rightarrow 0^+$. The remaining denominator of the integrand is exactly the factor multiplying t in the complex exponential. Differentiating both sides of the identity with respect to t and considering afterwards $\varepsilon' \rightarrow 0^+$ then gives

$$\frac{1}{f} \frac{d}{dt} \left[\langle \hat{B}_I(t) \rangle_{\text{n.eq.}} - \langle \hat{B} \rangle_{\text{eq.}} \right] = -2i\xi_{BA}(t).$$

Taking the initial condition at time $t = 0$ from Eq. (III.34), one finally obtains

$$\frac{1}{f} \left[\langle \hat{B}_I(t) \rangle_{\text{n.eq.}} - \langle \hat{B} \rangle_{\text{eq.}} \right] = \tilde{\chi}_{BA}(0) - 2i \int_0^t \xi_{BA}(t') dt' \quad \text{for } t > 0. \quad (\text{III.38})$$

Thus, the relaxation at $t > 0$ involves the integral of the Fourier transform of the spectral function.

III.2.4 Fluctuations

Taking $\hat{B} = \hat{A}$ and setting $\tau = 0$ in definitions (III.12) or (III.16), one finds

$$C_{AA}(\tau=0) = S_{AA}(\tau=0) = \langle \hat{A}^2 \rangle_{\text{eq.}}$$

If \hat{A} is centered, $\langle \hat{A} \rangle_{\text{eq.}} = 0$, then $\langle \hat{A}^2 \rangle_{\text{eq.}}$ is the variance of repeated measurements of the expectation value of \hat{A} , i.e. it is a measure of the *fluctuations* of the value taken by this observable.

When $\tau \neq 0$ or when \hat{B} and \hat{A} differ, $C_{BA}(\tau)$ and $S_{BA}(\tau)$ are no longer variances, but rather *covariances*—to be accurate, this holds if both \hat{A} and \hat{B} are centered—, which measure the degree of correlation between the two observables (see Appendix B.4.1).

⁽⁴⁴⁾or rather, to be precise, the product $\beta K_{BA}(t)$, which he denotes by $\Phi_{BA}(t)$.