III.3.2 Properties and relations of the time-correlation functions

III.3.2 a Properties of the time-correlation functions

We now list a few properties of the various time-correlation functions, without providing their respective proofs, starting with the symmetric and canonical correlation functions.[49]

- $S_{BA}(0) = S_{AB}(0) \quad , \quad K_{BA}(0) = K_{AB}(0);$ (III.44a)
- $S_{BA}(\tau) = S_{AB}(-\tau) \quad , \quad K_{BA}(\tau) = K_{AB}(-\tau);$ (III.44b)

  in particular $S_{AA}(\tau) = S_{AA}(-\tau) \quad , \quad K_{AA}(\tau) = K_{AA}(-\tau),$ (III.44c)

that is, S_{AA} and K_{AA} are even functions.
Note that similar properties do not hold for C_{BA} when $\hat{B} \neq \hat{A}$. However, one still has

$$C_{AA}(\tau) = C_{AA}(-\tau). \tag{III.44d}$$

Considering now complex conjugation, one finds [cf. Eq. (III.15)]

- $S_{BA}(\tau)^* = S_{A^\dagger B^\dagger}(-\tau) = S_{B^\dagger A^\dagger}(\tau) \quad , \quad K_{BA}(\tau)^* = K_{A^\dagger B^\dagger}(-\tau) = K_{B^\dagger A^\dagger}(\tau);$ (III.45a)
- if $\hat{A} = \hat{A}^\dagger$ and $\hat{B} = \hat{B}^\dagger$, $S_{BA}(\tau)$ and $K_{BA}(\tau)$ are real numbers; (III.45b)

  in particular for $\hat{B} = \hat{A}^\dagger = \hat{A}$, $S_{AA}(0)$ and $K_{AA}(0)$ are positive real numbers. (III.45c)

The latter property for Hermitian operators $\hat{A}$ also holds for $C_{AA}(0)$.
Given the antisymmetrization in the definition of $\xi_{BA}(\tau)$, the corresponding properties differ:

- $\xi_{BA}(0) = \xi_{AB}(0) = 0;$ (III.46a)
- $\xi_{BA}(\tau) = -\xi_{AB}(-\tau);$ (III.46b)

  in particular ξ_{AA} is odd: $\xi_{AA}(\tau) = -\xi_{AA}(-\tau),$ (III.46c)

Turning to complex conjugation, one finds

- $\xi_{BA}(\tau)^* = \xi_{A^\dagger B^\dagger}(-\tau) = -\xi_{B^\dagger A^\dagger}(\tau);$ (III.47a)
- if $\hat{A} = \hat{A}^\dagger$ and $\hat{B} = \hat{B}^\dagger$, $\xi_{BA}(\tau)$ is purely imaginary; . (III.47b)

We shall come back to property (III.46b) in § III.3.5, in which we shall take into account the specific behavior of the operators $\hat{A}$, $\hat{B}$ under time reversal.

III.3.2 b Interrelations between time-correlation functions

The explicit expression (III.26) of the generalized susceptibility shows that it is simply related to the inverse Fourier transform (III.19) of the spectral density according to

$$\boxed{\chi_{BA}(\tau) = 2\mathrm{i}\Theta(\tau)\,\xi_{BA}(\tau).} \tag{III.48}$$

Since $\chi_{BA}(\tau)$, which was defined for Hermitian operators only, is real-valued (see last remark of § III.1.2 a), one recovers property III.47b.

Let us define an operator $\hat{\dot{A}}$ by the relation

$$\hat{\dot{A}} \equiv \frac{1}{\mathrm{i}\hbar}\big[\hat{A}, \hat{H}_0\big], \tag{III.49}$$

i.e. such that its matrix elements are given by $(\dot{A})_{nn'} = (E_{n'} - E_n)A_{nn'}/\mathrm{i}\hbar = \mathrm{i}\omega_{nn'}A_{nn'}$ in the

[49] The properties involving C_{BA}, S_{BA} or ξ_{BA} can be read at once from their definitions (III.12) resp. (III.16), or invoking their respective spectral representations. Those pertaining to K_{BA} can be shown with the help of the decomposition (III.23), in particular using the invariance of the ratio under the exchange $n \leftrightarrow n'$.

energy-eigenstates basis. If $\hat{A}$ is an observable, then $\dot{\hat{A}}$ coincides with the value taken at $t = 0$ by the derivative $\mathrm{d}\hat{A}_{\mathrm{I}}(t)/\mathrm{d}t$ for a system evolving with $\hat{H}_0$ only, i.e. in the absence of external perturbation.

Replacing $\hat{A}$ by $\dot{\hat{A}}$ in the spectral form (III.23) of Kubo's correlation function, one finds

$$K_{B\dot{A}}(\tau) = \mathrm{i}\sum_{n,n'} \frac{\pi_n - \pi_{n'}}{\beta\hbar} B_{nn'} A_{n'n} \mathrm{e}^{-\mathrm{i}\omega_{n'n}\tau},$$

i.e.

$$K_{B\dot{A}}(\tau) = \frac{2\mathrm{i}}{\beta} \xi_{BA}(\tau). \tag{III.50}$$

In turn, relation (III.48), becomes

$$\boxed{\chi_{BA}(\tau) = \beta K_{B\dot{A}}(\tau)\Theta(\tau).} \tag{III.51}$$

This relation is sometimes referred to as *Kubo formula*, since in his original article [33] Kubo expressed the linear response to a perturbation with the help of $\beta K_{B\dot{A}}(\tau)$ instead of the retarded propagator $\chi_{BA}(\tau)$ used in § III.1.2.

Identifying the right-hand sides of Eqs. (III.37) and (III.38) and differentiating the resulting relation with respect to time, one finds

$$\frac{\mathrm{d}K_{BA}(\tau)}{\mathrm{d}\tau} = -\frac{2\mathrm{i}}{\beta} \xi_{BA}(\tau).$$

Equation (III.50) then yields

$$\frac{\mathrm{d}K_{BA}(\tau)}{\mathrm{d}\tau} = -K_{B\dot{A}}(\tau). \tag{III.52}$$

III.3.5 Onsager relations

Using the symmetries of a problem often allows one to deduce interesting relations as well as simplifications. We discuss here a first example, in the case of symmetry under time reversal. A further example will be given illustrated on an explicit example in § **??**, when discussing quantum Brownian motion.

Equation (III.46b) relates ξ_{BA}, i.e. the response of $\hat{B}$ to a excitation coupled to $\hat{A}$, to ξ_{AB}, which describes the "reciprocal" situation of the change in the expectation value of $\hat{A}$ induced by a perturbation coupling to $\hat{B}$. More precisely, it is a relation between $\xi_{BA}(t)$ and $\xi_{AB}(-t)$, that is with reversed time direction, which is slightly unsatisfactory.

To obtain an equation relating $\xi_{BA}(t)$ and $\xi_{AB}(t)$, with the same time direction in both correlation functions, one needs to introduce the time reversal operator $\hat{\mathscr{T}}$ and to discuss the behavior of the various observables under its operation.

III.3.5 a Time reversal in quantum mechanics

Accordingly, let us briefly recall some properties of the operator $\hat{\mathscr{T}}$ which represents the action of the time-reversal operation on spinless particles.[54] These follow from the fact that $\hat{\mathscr{T}}$ is an *antiunitary* operator, i.e. an antilinear operator whose adjoint equals its inverse.

Let $\hat{\mathcal{A}}$ denote an antilinear operator. If $|1\rangle$, $|2\rangle$ are two kets of the Hilbert space $\mathscr{H}$ on which $\hat{\mathcal{A}}$ is acting, and λ_1, λ_2 two complex constants, one has

$$\hat{\mathcal{A}}\big(\lambda_1|1\rangle + \lambda_2|2\rangle\big) = \lambda_1^*\,\hat{\mathcal{A}}\,|1\rangle + \lambda_2^*\,\hat{\mathcal{A}}\,|2\rangle. \tag{III.72a}$$

That is, if $\lambda \in \mathbb{C}$

$$\hat{\mathcal{A}}\lambda = \lambda^*\hat{\mathcal{A}}. \tag{III.72b}$$

[54] For further details, see e.g. Messiah [29] Chapter 15, in particular Secs. 3–5 & 15–22.

If $\langle\phi|$ is a bra (belonging to the dual space to $\mathscr{H}$), the action of $\hat{\mathcal{A}}$ on $\langle\phi|$ defines a new bra $\langle\phi|\hat{\mathcal{A}}$ such that for any ket $|\psi\rangle$, one has the identity

$$\big(\langle\phi|\,\hat{\mathcal{A}}\big)|\psi\rangle = \Big[\langle\phi|\big(\hat{\mathcal{A}}\,|\psi\rangle\big)\Big]^*. \tag{III.72c}$$

Note that the brackets cannot be dropped, contrary to the case of linear operators: one must specify whether $\hat{\mathcal{A}}$ acts on the ket or on the bra.

The adjoint operator $\hat{\mathcal{A}}^\dagger$ of the antilinear operator $\hat{\mathcal{A}}$ is such that for all $|\phi\rangle$, $\hat{\mathcal{A}}^\dagger|\phi\rangle$ is the ket conjugate to the bra $\langle\phi|\hat{\mathcal{A}}$. For all $|\phi\rangle$, $|\psi\rangle$, the usual property of the scalar product reads

$$\langle\psi|\big(\hat{\mathcal{A}}^\dagger|\phi\rangle\big) = \Big[\big(\langle\phi|\hat{\mathcal{A}}\big)|\psi\rangle\Big]^*.$$

Comparing with Eq. (III.72c), this gives the relation

$$\langle\psi|\big(\hat{\mathcal{A}}^\dagger|\phi\rangle\big) = \langle\phi|\big(\hat{\mathcal{A}}\,|\psi\rangle\big). \tag{III.72d}$$

Eventually, the antiunitarity of $\hat{\mathscr{T}}$ means that it obeys the additional identity

$$\hat{\mathscr{T}}\hat{\mathscr{T}}^\dagger = \hat{\mathscr{T}}^\dagger\hat{\mathscr{T}} = \hat{\mathbb{1}}. \tag{III.72e}$$

It follows from this relation that if vectors $\{\,|\phi_n\rangle\}$ form an orthonormal basis, then so do the transformed vectors $\{\hat{\mathscr{T}}\,|\phi_n\rangle\}$, which will be denoted as $\{\,|\,\hat{\mathscr{T}}\phi_n\rangle\}$.

Signature of an operator under time reversal

Many operators $\hat{O}$ acting on a system transform in a simple way under time reversal, namely according to

$$\hat{\mathscr{T}}\hat{O}\hat{\mathscr{T}}^\dagger = \epsilon_O\hat{O} \quad \text{with } \epsilon_O = +1 \text{ or } -1. \tag{III.73}$$

ϵ_O is the *signature* of the operator $\hat{O}$ under time reversal.
For instance, time reversal does not modify positions, but changes velocities

$$\hat{\mathscr{T}}\hat{\vec{X}}\hat{\mathscr{T}}^\dagger = \hat{\vec{X}}, \qquad \hat{\mathscr{T}}\hat{\vec{V}}\hat{\mathscr{T}}^\dagger = -\hat{\vec{V}}, \tag{III.74}$$

that is $\epsilon_X = 1$, $\epsilon_V = -1$.

Consider now a system with Hamilton operator $\hat{H}$, assumed to be invariant under time reversal, i.e. $\hat{\mathscr{T}}\hat{H}\hat{\mathscr{T}}^\dagger = \hat{H}$. Let $\hat{O}_{\rm H}(t)$ denote the Heisenberg representation (II.36) of an observable $\hat{O}$; one may then write

$$\hat{\mathscr{T}}\,\hat{O}_{\rm H}(t)\hat{\mathscr{T}}^\dagger = \hat{\mathscr{T}}\,{\rm e}^{{\rm i}\hat{H}t/\hbar}\,\hat{O}\,{\rm e}^{-{\rm i}\hat{H}t/\hbar}\,\hat{\mathscr{T}}^\dagger = \hat{\mathscr{T}}\,{\rm e}^{{\rm i}\hat{H}t/\hbar}\,\hat{\mathscr{T}}^\dagger\hat{\mathscr{T}}\,\hat{O}\hat{\mathscr{T}}^\dagger\hat{\mathscr{T}}\,{\rm e}^{-{\rm i}\hat{H}t/\hbar}\,\hat{\mathscr{T}}^\dagger,$$

where the (anti)unitarity (III.72e) was used. Invoking now Eqs. (III.72b) and (III.73), and again the antiunitarity property yields the relation

$$\hat{\mathscr{T}}\,\hat{O}_{\rm H}(t)\hat{\mathscr{T}}^\dagger = {\rm e}^{-{\rm i}\hat{H}t/\hbar}\,\epsilon_O\hat{O}\,{\rm e}^{{\rm i}\hat{H}t/\hbar} = \epsilon_O\hat{O}_{\rm H}(-t), \tag{III.75}$$

which shows that the time reversal operator acts on operators as it is supposed to, inversing the direction of time evolution.

Remark: In the presence of an external magnetic field $\vec{\mathscr{B}}_{\rm ext.}$, the Hamiltonian $\hat{H}$ is not invariant under time reversal. As a matter of fact, the magnetic field couples to operators of the system with signature -1, as for instance the velocity of particles or their spins, so that the transformed of $\hat{H}$ under time reversal corresponds to the Hamiltonian of the same system in presence of the opposite magnetic field $-\vec{\mathscr{B}}_{\rm ext.}$:

$$\hat{\mathscr{T}}\,\hat{H}\big[\vec{\mathscr{B}}_{\rm ext.}\big]\hat{\mathscr{T}}^\dagger = \hat{H}\big[-\vec{\mathscr{B}}_{\rm ext.}\big]. \tag{III.76}$$

III.3.5 b Behavior of correlation functions under time reversal

Let us come back to the generic setup of this Chapter, namely to a system with unperturbed Hamiltonian $\hat{H}_0$. We assume that the latter is invariant under time reversal, so that $\hat{H}_0$ and $\hat{\mathscr{T}}$ commute. As a consequence, the canonical equilibrium density operator $\hat{\rho}_{\text{eq.}}$ also commutes with the time reversal operator.

Considering operators $\hat{A}$ and $\hat{B}$ with definite signatures under time reversal and their respective Heisenberg representations (III.3) with respect to $\hat{H}_0$, we can compute the equilibrium expectation value $\big\langle \hat{B}_{\text{I}}(t)\hat{A}\big\rangle_{\text{eq.}}$:

$$\text{Tr}\big[\hat{\rho}_{\text{eq.}}\hat{B}_{\text{I}}(t)\hat{A}\big] = \sum_n \langle\phi_n|\hat{\rho}_{\text{eq.}}\hat{B}_{\text{I}}(t)\hat{A}|\phi_n\rangle = \sum_n \langle\phi_n|\Big(\hat{\mathscr{T}}^\dagger\hat{\mathscr{T}}\hat{\rho}_{\text{eq.}}\hat{\mathscr{T}}^\dagger\hat{\mathscr{T}}\hat{B}_{\text{I}}(t)\hat{\mathscr{T}}^\dagger\hat{\mathscr{T}}\hat{A}\hat{\mathscr{T}}^\dagger\hat{\mathscr{T}}|\phi_n\rangle\Big).$$

Using the identities $\hat{\mathscr{T}}\hat{\rho}_{\text{eq.}}\hat{\mathscr{T}}^\dagger = \hat{\rho}_{\text{eq.}}$, $\hat{\mathscr{T}}\hat{B}_{\text{I}}(t)\hat{\mathscr{T}}^\dagger = \epsilon_B\hat{B}_{\text{I}}(-t)$ and $\hat{\mathscr{T}}\hat{A}\hat{\mathscr{T}}^\dagger = \epsilon_A\hat{A}$ in the right-most member of the equation, this becomes

$$\begin{aligned}\big\langle \hat{B}_{\text{I}}(t)\hat{A}\big\rangle_{\text{eq.}} &= \epsilon_A\epsilon_B\sum_n \langle\phi_n|\Big(\hat{\mathscr{T}}^\dagger\hat{\rho}_{\text{eq.}}\hat{B}_{\text{I}}(-t)\hat{A}|\hat{\mathscr{T}}\phi_n\rangle\Big)\\ &= \epsilon_A\epsilon_B\sum_n \langle\hat{\mathscr{T}}\phi_n|\hat{A}^\dagger\hat{B}_{\text{I}}(-t)^\dagger\hat{\rho}_{\text{eq.}}\Big(\hat{\mathscr{T}}|\phi_n\rangle\Big),\end{aligned}$$

where the second identity follows from applying property (III.72d) with $|\phi\rangle = \hat{\rho}_{\text{eq.}}\hat{B}_{\text{I}}(-t)\hat{A}|\hat{\mathscr{T}}\phi_n\rangle$, $\hat{\mathcal{A}} = \hat{\mathscr{T}}$, and $\langle\psi| = \langle\phi_n|$, while using the hermiticity of $\hat{\rho}_{\text{eq.}}$. The term $\big(\hat{\mathscr{T}}|\phi_n\rangle\big)$ can then be rewritten as $|\hat{\mathscr{T}}\phi_n\rangle$. Since the vectors $\{\hat{\mathscr{T}}|\phi_n\rangle\}$ form an orthogonal basis, the sum on the right-hand side actually represents a trace

$$\big\langle \hat{B}_{\text{I}}(t)\hat{A}\big\rangle_{\text{eq.}} = \epsilon_A\epsilon_B\text{Tr}\big[\hat{A}^\dagger\hat{B}_{\text{I}}(-t)^\dagger\hat{\rho}_{\text{eq.}}\big] = \epsilon_A\epsilon_B\big\langle\hat{A}^\dagger\hat{B}_{\text{I}}(-t)^\dagger\big\rangle_{\text{eq.}}.$$

If both $\hat{A}$ and $\hat{B}$ are Hermitian and using stationarity, this gives

$$\big\langle \hat{B}_{\text{I}}(t)\hat{A}\big\rangle_{\text{eq.}} = \epsilon_A\epsilon_B\big\langle\hat{A}_{\text{I}}(t)\hat{B}\,\big\rangle_{\text{eq.}}.$$

One similarly shows $\langle\hat{A}\hat{B}_{\text{I}}(t)\rangle_{\text{eq.}} = \epsilon_A\epsilon_B\langle\hat{B}\hat{A}_{\text{I}}(t)\rangle_{\text{eq.}}$, which leads to the *reciprocity relations*

$$\xi_{BA}(t) = \epsilon_A\epsilon_B\,\xi_{AB}(t), \tag{III.77a}$$

and after Fourier transforming

$$\boxed{\tilde{\xi}_{BA}(\omega) = \epsilon_A\epsilon_B\,\tilde{\xi}_{AB}(\omega).} \tag{III.77b}$$

This result constitutes the generalization of the Onsager reciprocal relations introduced in §I.2.2 b, which are the zero-frequency limit of the second relation here (see also §III.4.1 a).

When the system is in an external magnetic field $\vec{\mathscr{B}}_{\text{ext.}}$, one shows with the help of Eq. (III.76) that relation (III.77b) generalizes to

$$\tilde{\xi}_{BA}(\omega,\vec{\mathscr{B}}_{\text{ext.}}) = \epsilon_A\epsilon_B\,\tilde{\xi}_{AB}(\omega,-\vec{\mathscr{B}}_{\text{ext.}}). \tag{III.78}$$

Starting from this relation or, in the absence of magnetic field, from Eq. (III.77b), one easily derives similar relations for the other spectral representations $\tilde{\chi}_{BA}(\omega)$, $\tilde{S}_{BA}(\omega)$, $\tilde{K}_{BA}(\omega)$.

Remarks:

∗ In combination with relation (III.54b), Eq. (III.77) shows that the spectral function $\tilde{\xi}_{BA}(\omega)$ is real and odd when $\epsilon_A\epsilon_B = 1$, or purely imaginary and even if $\epsilon_A\epsilon_B = -1$.

∗ Using relation (III.48) between the linear response function and the inverse Fourier transform of the spectral function, one deduces from Eq. (III.77) the identities

$$\chi_{BA}(t) = \epsilon_A\epsilon_B\,\chi_{AB}(t) \quad , \quad \tilde{\chi}_{BA}(\omega) = \epsilon_A\epsilon_B\,\tilde{\chi}_{AB}(\omega). \tag{III.79}$$

Accordingly, relation (III.57) becomes

$$\tilde{\xi}_{BA}(\omega) = \frac{1}{2\mathrm{i}}\big[\tilde{\chi}_{BA}(\omega) - \epsilon_A\epsilon_B\,\tilde{\chi}_{BA}(\omega)^*\big].$$

If observables $\hat{A}$ and $\hat{B}$ have the same parity under time reversal, then $\tilde{\xi}_{BA}(\omega)$ is the imaginary part of $\tilde{\chi}_{BA}(\omega)$, as in the case $\hat{B} = \hat{A}^\dagger$ [Eq. (III.58)]. On the other hand, if they have opposite parities, then the above identity reads $\tilde{\xi}_{BA}(\omega) = -\mathrm{i}\,\mathrm{Re}\,\tilde{\chi}_{BA}(\omega)$: the dissipative part of the susceptibility is now its real part.

Accordingly, the rather standard notation $\chi''_{BA}(\tau)$ for the function called in these notes $\xi_{BA}(\tau)$ can be misleading in a twofold way: firstly, despite the double-primed notation, it is *not* the imaginary part of the retarded propagator $\chi_{BA}(\tau)$ even though $\tilde{\chi}''_{BA}(\omega)$ is that of $\tilde{\chi}_{BA}(\omega)$. Secondly, $\chi''_{BA}(\tau)$ is the inverse Fourier transform of $\tilde{\chi}''_{BA}(\omega)$ only if $\hat{A}$ and $\hat{B}$ behave similarly under time reversal.

III.4 Examples and applications

The overall presentation of this Section is missing.

A further example will be given in Sec. IV.4.

III.4.1 Green–Kubo relation

An important application of the formalism of linear response is the calculation of the transport coefficients which appear in the phenomenological constitutive relations of non-equilibrium thermodynamics.

III.4.1 a Linear response revisited

Under consideration of relation (III.48) or (III.51) and dropping the nonlinear terms, the Kubo formula (III.8) can be recast as either

$$\langle \hat{B}_{\rm I}(t)\rangle_{\text{n.eq.}} = \langle \hat{B}\,\rangle_{\text{eq.}} + 2{\rm i}\int_0^\infty \xi_{BA}(\tau)\, f(t-\tau)\,{\rm d}\tau \tag{III.83}$$

or equivalently

$$\langle \hat{B}_{\rm I}(t)\rangle_{\text{n.eq.}} = \langle \hat{B}\,\rangle_{\text{eq.}} + \int_0^\infty \beta K_{B\dot{A}}(\tau)\, f(t-\tau)\,{\rm d}\tau, \tag{III.84}$$

where the latter is in fact the form originally given by Kubo.

Let us assume that the expectation value of $\hat{B}$ at equilibrium vanishes: for instance, $\hat{B}$ is a flux as introduced in Chapter I. To emphasize this interpretation, we denote the responding observable by $\hat{\mathcal{J}}_b$, instead of $\hat{B}$. Accordingly, to increase the similarity with Sec. I.2, we call the generalized force $\mathscr{F}_a(t)$ instead of $f(t)$, and we rename $\hat{A}_a$ the observable coupling to $\mathscr{F}_a(t)$.

Fourier transforming relations (III.83) or (III.84) leads to

$$\langle \tilde{\hat{\mathcal{J}}}_b(\omega)\rangle_{\text{n.eq.}} = L_{ba}(\omega)\tilde{\mathscr{F}}_a(\omega), \tag{III.85a}$$

where we also adopted a new notation for the susceptibility:

$$L_{ba}(\omega) \equiv \beta\int_0^\infty K_{\mathcal{J}_b\dot{A}_a}(\tau)\,{\rm e}^{{\rm i}\omega\tau}\,{\rm d}\tau = 2{\rm i}\int_0^\infty \xi_{\mathcal{J}_bA_a}(\tau)\,{\rm e}^{{\rm i}\omega\tau}\,{\rm d}\tau. \tag{III.85b}$$

Summing over different generalized forces, whose effects simply add up at the linear approximation, the Fourier-transformed Kubo formula (III.85a) is a straightforward generalization of Eq. (I.31) accounting for frequency dependent fluxes and affinities. The real novelty is that the "generalized kinetic coefficient" $L_{ba}(\omega)$ is no longer a phenomenological factor as in Sec. I.2: instead, there is now an explicit formula to compute it using time-correlation functions at equilibrium of the system, Eq. (III.85b).

In Chapter I, the considered affinities and fluxes were implicitly quasi-static—the gradients of intensive thermodynamic quantities were time-independent—, which is the regime for which transport coefficients are defined. For instance, the electric conductivity $\sigma_{\text{el.}}$ is defined as the proportionality factor between a constant electric field and the ensuing direct current. Accordingly, the kinetic coefficients L_{ba} in the constitutive relation (I.31) are actually the zero-frequency limits of the corresponding susceptibilities:

$$L_{ba} = \lim_{\omega\to 0}\frac{1}{k_BT}\int_0^\infty K_{\mathcal{J}_b\dot{A}_a}(\tau)\,{\rm e}^{{\rm i}\omega\tau}\,{\rm d}\tau = \frac{1}{k_BT}\int_0^\infty K_{\mathcal{J}_b\dot{A}_a}(\tau)\,{\rm d}\tau. \tag{III.86}$$

This constitutes the general form of the *Green*[(ax)]*–Kubo-relation* [40, 41, 33].

[(ax)] M. S. Green, 1922–1979

III.4.1 b Example: electric conductivity

As example of application of the Green–Kubo-relation, consider a system made of electrically charged particles, with charges q_i, submitted to a uniform classical external electric field $\vec{\mathscr{E}}(t)$, which plays the role of the generalized force. This field, which derives from an electrostatic potential $\Phi(\vec{r}) = -\vec{r}\cdot\vec{\mathscr{E}}(t)$, perturbs the Hamiltonian, coupling to the positions of the charge carriers:

$$\hat{W}(t) = -\sum_i q_i \Phi\big(\hat{\vec{r}}_i\big) = \vec{\mathscr{E}}(t)\cdot\hat{\vec{D}} \quad \text{where} \quad \hat{\vec{D}} \equiv \sum_i q_i \hat{\vec{r}}_i$$

with $\hat{\vec{r}}_i$ the position operator of the i-th particle.

Quite obviously, we are interested in the electric current due to this perturbation, namely

$$\hat{\vec{J}}_{\text{el.}}(t) \equiv \sum_i q_i \frac{\mathrm{d}\hat{\vec{r}}_i(t)}{\mathrm{d}t}.$$

In the notations of the present Chapter, $\hat{A}$ is the component of $\hat{\vec{D}}$ along the direction of $\vec{\mathscr{E}}$—let us for simplicity denote this component by $\hat{D}_z$—, while the role of $\hat{B}$ is played by any component $\hat{J}_{\text{el.},j}$ of $\hat{\vec{J}}_{\text{el.}}$. Additionally, one sees that $\hat{B} = \dot{\hat{A}}$ in the case $\hat{B} = \hat{J}_{\text{el.},z}$.

Focussing on the latter case, Kubo's linear response formula reads in Fourier space

$$\hat{J}_{\text{el.},z}(\omega) = \tilde{\chi}_{J_z D_z}(\omega)\mathscr{E}_z(\omega) \equiv \sigma_{zz}(\omega)\mathscr{E}_z(\omega),$$

where for obvious reasons we have introduced for the relevant generalized susceptibility the alternative notation $\sigma_{zz}(\omega)$. The zero-frequency limit of σ_{zz} is the electric conductivity, which according to the Green–Kubo-relation (III.86) is given by

$$\sigma_{\text{el.}} = \frac{1}{k_B T}\int_0^\infty K_{J_z J_z}(\tau)\,\mathrm{d}\tau,$$

i.e. by the integral of the time-autocorrelation function of the component of the electric current along the direction of the electric field.

Let us again emphasize that given a microscopic model of the system, the canonical correlation function can be calculated, which then allows one to *compute* the electric conductivity, which in § I.2.3 c was a mere phenomenological coefficient.