Chapter III

Linear response theory

When the Hamiltonian of a system—be it described classically or quantum mechanically—is known, the time evolution of its observables is fixed and obeys the appropriate deterministic equation (II.16) or (II.38). Consider for instance a classical system, governed by a (time-independent) Hamilton function H_0, which encodes all interactions between the system particles. If $O(t)$ is one of the observables of the system, there is the same amount of information in its values at two successive times t and t'.

On the other hand, if H_0 is unknown, measuring both $O(t)$ and $O(t')$ and correlating their values is likely to improve the knowledge on the system. For the correlation to be meaningful—on the theoretical side, one pair of successive values represent only one glimpse into a realization of a stochastic process; and on the other side, experimental uncertainties cannot be discarded—, the measurements have to be repeated many times in similar conditions[(40)] and their results averaged over. In this way one builds a *time correlation function* $\langle O(t)O(t')\rangle$. Technically, the "similar conditions" amount to an identical macrostate of the system, the state of choice being that of thermodynamic equilibrium, which leads to correlators $\langle O(t)O(t')\rangle_{\text{eq.}}$.

The procedure can be repeated for other observables, and one can even correlate the values taken at two instants by two different observables. This potentially leads to plenty of time-correlation functions, each of which encode some information about the system. More precisely, correlators built at thermodynamic equilibrium allow one to access the coefficients that characterize out-of-equilibrium states of the system. Since many kinds of departure from equilibrium are possible, one has to consider several correlation functions to describe them—in contrast to the equilibrium state, whose properties are entirely contained in the relevant partition function.

Restricting the discussion to near-equilibrium macrostates, the deviation of their properties from the equilibrium ones can be approximated as being linear in some appropriate small perturbation(s). This is similar to the assumed linearity of the fluxes in the affinities of Sec. I.2. Accordingly, each of the transport coefficients introduced in that chapter can be expressed in terms of the integral of a given correlation function, as we shall illustrate in Sec. III.4. Before coming to that point, we first introduce time-correlation functions for homogeneous quantum-mechanical systems in Sec. III.1. We then discuss the meaning of these functions (Sec. III.2) and consider some of their more formal aspects (Sec. III.3). This will in particular allow us to derive the Onsager relations, which were introduced as postulates in §I.2.2 b. Eventually, we discuss in two appendices the important generalization to non-uniform systems (Sec. III.A) as well as the classical theory of linear response (Sec. III.B).

Before going any further, let us emphasize that the formalism of linear response developed hereafter, even though limited to small departures from equilibrium, is not a phenomenological description, but a theory, based on exact quantum mechanical equations—which are dealt with perturbatively. As thus, the results discussed in Sec. III.3 constitute stringent constraints for the parameters used in models.

(40) That is, for identically prepared systems.

III.1 Time correlation functions

In this section, we introduce various functions relating the values taken by two observables A and B of a macroscopic system at thermodynamic equilibrium. We mostly consider the case of a quantum mechanical system, specified in § III.1.1, in which case the observables are represented by Hermitian operators $\hat{A}$ and $\hat{B}$. For the sake of simplicity, we first consider observables associated to physical quantities which are uniform across the system under study, so that they do not depend on position, only on time. The generalization to non-uniform phenomena will be shortly presented in § III.A.1, and linear response in classical systems discussed in § III.B.1.

Since the operators $\hat{A}$ and $\hat{B}$ generally do not commute with each other, there are several possible choices of correlation functions, which we define in § III.1.2–III.1.5. At the same time, we introduce their respective Fourier transforms and we indicate a few straightforward properties. However, we postpone the discussion of the physical content of each correlation function to next section, while their at times important mathematical properties will be studied at greater length in Sec. III.3.

III.1.1 Assumptions and notations

Consider an isolated quantum-mechanical system, governed by the Hamilton operator $\hat{H}_0$—acting on a Hilbert space which we need not specify—, whose eigenvalues and eigenstates are respectively denoted as $\{E_n\}$ and $\{\,|\phi_n\rangle\}$:

$$\hat{H}_0\,|\phi_n\rangle = E_n\,|\phi_n\rangle. \tag{III.1}$$

The system is assumed to be initially at thermodynamic equilibrium at temperature T. The associated density operator $\hat{\rho}_{\text{eq.}}$ thus reads

$$\hat{\rho}_{\text{eq.}} = \frac{1}{Z(\beta)}\,\mathrm{e}^{-\beta\hat{H}_0}, \quad \text{with} \quad Z(\beta) = \mathrm{Tr}\,\mathrm{e}^{-\beta\hat{H}_0} \text{ and } \beta = \frac{1}{k_BT}. \tag{III.2a}$$

This canonical density operator is quite obviously diagonal in the basis $\{\,|\phi_n\rangle\}$

$$\langle\phi_n|\,\hat{\rho}_{\text{eq.}}|\phi_{n'}\rangle = \frac{1}{Z(\beta)}\,\mathrm{e}^{-\beta E_n}\,\delta_{nn'} \equiv \pi_n\,\delta_{nn'}, \tag{III.2b}$$

where the diagonal elements π_n represent the equilibrium populations of the energy eigenstates.

Let $\hat{O}$ denote a time-independent operator on the Hilbert space of the system. In the Heisenberg representation with respect to $\hat{H}_0$, it is represented by the operator [this is relation (II.39), here with $t_0 = 0$[(41)]]

$$\hat{O}_{\mathrm{I}}(t) = \mathrm{e}^{\mathrm{i}\hat{H}_0t/\hbar}\,\hat{O}\,\mathrm{e}^{-\mathrm{i}\hat{H}_0t/\hbar}, \tag{III.3}$$

where instead of H we used the subscript I, for "interaction picture", anticipating the fact that we shall often consider perturbations of the system. The expectation value of the observable in the equilibrium (macro)state reads

$$\big\langle\hat{O}_{\mathrm{I}}(t)\big\rangle_{\text{eq.}} = \mathrm{Tr}\big[\hat{\rho}_{\text{eq.}}\hat{O}_{\mathrm{I}}(t)\big] = \mathrm{Tr}\big[\hat{\rho}_{\text{eq.}}\hat{O}\big], \tag{III.4}$$

where the second identity follows from the invariance of the trace under cyclic permutations and the commutativity of $\hat{\rho}_{\text{eq.}}$ and $\hat{H}_0$. That is, $\langle\hat{O}_{\mathrm{I}}(t)\rangle_{\text{eq.}}$ is actually independent of time, which is to be expected since the system is assumed to be at equilibrium, so that its characteristics are stationary.

Remark: Equation (III.3) gives $\hat{O}_{\mathrm{I}}(t=0) = \hat{O}$, which will allow us to write $\hat{O}$ instead of $\hat{O}_{\mathrm{I}}(0)$.[(41)] Accordingly, we will from now on write $\big\langle\hat{O}\big\rangle_{\text{eq.}}$ instead of $\big\langle\hat{O}_{\mathrm{I}}(t)\big\rangle_{\text{eq.}}$.

[(41)] The reader may check that adopting another choice for t_0 does not make any difference, except that it changes the reference point where $\hat{O}_{\mathrm{I}}(t)$ coincides with the Schrödinger-representation $\hat{O}$.

Let $O_{nn'} \equiv \langle\phi_n|\,\hat{O}\,|\phi_{n'}\rangle$ denote the matrix elements of the observable $\hat{O}$ in the basis $\{\,|\phi_n\rangle\}$. Since the latter is formed of eigenstates of the Hamilton operator, one readily finds that the matrix elements of $\hat{O}_{\rm I}(t)$ are

$$[O_{\rm I}(t)]_{nn'} = O_{nn'}\,{\rm e}^{{\rm i}(E_n-E_{n'})t/\hbar} = O_{nn'}\,{\rm e}^{{\rm i}\omega_{nn'}t}, \tag{III.5}$$

where in the second identity we have introduced the Bohr[(ai)] (angular) frequencies

$$\omega_{nn'} \equiv \frac{E_n - E_{n'}}{\hbar} \tag{III.6}$$

of the system.

III.1.2 Linear response function and generalized susceptibility

The system initially at equilibrium is submitted to a small uniform excitation, which we shall also refer to as perturbation, described by a time-dependent additional term

$$\hat{W}(t) = -f(t)\,\hat{A}. \tag{III.7}$$

in the Hamiltonian in Schrödinger representation. Here $\hat{A}$ is an observable of the system and $f(t)$ a given classical function of t, which is assumed to vanish for $t \to -\infty$. $f(t)$ is sometimes referred to as the *generalized force* conjugate to $\hat{A}$—which is then the corresponding "generalized displacement".

In the limit $t \to -\infty$, the system is thus in the macroscopic state (III.2), and the excitation (III.7) drives it out of equilibrium; if the perturbation is weak, the resulting departure will remain small. The various observables $\hat{B}$ of the system then acquire expectation values $\langle\hat{B}_{\rm I}(t)\rangle_{\rm n.eq.}$ which will in general differ from their respective equilibrium values $\langle\hat{B}_{\rm I}(t)\rangle_{\rm eq.}$ as given by Eq. (III.4).

Remarks:

∗ In this section, since $\hat{A}$ and $\hat{B}$ are observables, they are Hermitian operators. To ensure the hermiticity of the Hamiltonian, $f(t)$ should be real-valued. In § III.1.3–III.1.5, we shall more generally consider time-correlation functions of operators that need not necessarily be Hermitian.

∗ Excitations which can be described by an extra term in the Hamiltonian, as we consider here, are often referred to as *mechanical*, in opposition to *thermal* disturbances—as e.g. a temperature gradient, which cannot trivially be rendered by a shift in the Hamiltonian. The former are driven by external forces, which an experimenter may control, while the latter rather arise from internal, "thermodynamical" forces. It is sometimes also possible to deal with thermal excitations by engineering theoretical forces which allows one to use the formalism developed for mechanical perturbations.

III.1.2 a Linear response function

To describe the linear response of the system to the perturbation (III.7), one introduces the *(linear) response function* χ_{BA} such that

$$\big\langle\hat{B}_{\rm I}(t)\big\rangle_{\rm n.eq.} = \big\langle\hat{B}\,\big\rangle_{\rm eq.} + \int_{-\infty}^{\infty}\chi_{BA}(t-t')\,f(t')\,{\rm d}t' + \mathcal{O}(f^2). \tag{III.8}$$

In this definition, the upper boundary of the integral extends to $+\infty$, i.e. formally involves the generalized force in the future of the time t at which the effect $\langle\hat{B}_{\rm I}(t)\rangle_{\rm n.eq.}$ is considered, which seems to violate causality. To restore the latter, one may either restrict the integral to the range $-\infty < t' \leq t$—which is indeed what comes out of the explicit calculation of the linear response, as we shall see in § III.2.1 below—, or define the response function such that it vanishes for $t' > t$, i.e. $\tau \equiv t - t' < 0$, as we shall do:

$$\chi_{BA}(\tau) = 0 \quad \text{for} \quad \tau < 0. \tag{III.9}$$

(ai) N. Bohr, 1885–1962

To emphasize the causality, the linear response function χ_{BA} is often called *after-effect function*.

If the perturbation $f(t)$ is an impulse, i.e. $f(t) \propto \delta(t)$, relation (III.8) shows that the linear response $\langle \hat{B}_{\rm I}(t)\rangle_{\rm n.eq.} - \langle \hat{B}\rangle_{\rm eq.}$ is directly proportional to $\chi_{BA}(t)$. Accordingly, χ_{BA} is also referred to as *impulse response function*—in particular in signal theory—or, to account simultaneously for its causality property, *retarded Green*[(aj)] *function* or *retarded propagator*.

Remarks:

∗ Equation (III.8) represents a linear (in the regime of small excitations), causal, and time-translation invariant relation between an "input" $f(t')$ and an "output" $\langle \hat{B}_{\rm I}(t)\rangle_{\rm n.eq.} - \langle \hat{B}\rangle_{\rm eq.}$. The response function χ_{BA} thus plays the role of a *linear filter*.

∗ The response described by the formula (III.8) is obviously no longer "Markovian", as were the relations between fluxes and affinities considered in Sec. I.2. The memoryless case could a priori be recovered by taking the response function $\chi_{BA}(\tau)$ proportional to $\delta(\tau)$, yet we shall later see that such a behavior cannot be accommodated within linear response theory, for it leads to the violation of important relations (see the "Comparison" paragraph at the end of § IV.4.1 b).

∗ The dependence of the linear response function on the observables $\hat{A}$ and $\hat{B}$ is readily obtained, yet we postpone its derivation for later (§ III.2.1). Without any calculation, it should be clear to the reader that if the departure from equilibrium $\langle \hat{B}_{\rm I}(t)\rangle_{\rm n.eq.} - \langle \hat{B}\rangle_{\rm eq.}$ is to be linear in the perturbation, i.e. of order $\mathcal{O}(f)$, then Eq. (III.8) implies that χ_{BA} should be of order $\mathcal{O}(f^0)$, that is, χ_{BA} depends only on *equilibrium* quantities.

∗ The causality property (III.9) encoded in the linear response functions will strongly constraint its Fourier transform, as we shall see in § III.3.1.

∗ Relation (III.8) is sometimes called *Kubo*[(ak)] *formula*, although the denomination is also often attached to another, equivalent form of the equation [see Eq. (III.51) below].

∗ Since $\hat{B}$ is a Hermitian operator, its expectation values in or out of equilibrium are real numbers. Assuming $f(t) \propto \delta(t)$, one then finds that the retarded propagator $\chi_{BA}(\tau)$ is real-valued.

III.1.2 b Generalized susceptibility

The integral in the defining relation (III.8) is a time convolution, which suggests Fourier transforming to frequency space.
Accordingly, one introduces the Fourier transform of the response function as

$$\tilde{\chi}_{BA}(\omega) = \lim_{\varepsilon\to 0^+} \int_{-\infty}^{\infty} \chi_{BA}(\tau)\, {\rm e}^{{\rm i}\omega\tau}\, {\rm e}^{-\varepsilon\tau}\, {\rm d}\tau, \tag{III.10a}$$

where an exponential factor ${\rm e}^{-\varepsilon\tau}$ with $\varepsilon > 0$ was inserted for the sake of ensuring the convergence—as we shall see later, one can easily check that $\chi_{BA}(\tau)$ does not diverge as $\tau \to \infty$, so that this factor is sufficient. $\tilde{\chi}_{BA}(\omega)$ is referred to as *(generalized) susceptibility*, *generalized admittance* or *frequency response function*.
The inverse Fourier transform reads[(42)]

$$\chi_{BA}(\tau) = \int_{-\infty}^{\infty} \tilde{\chi}_{BA}(\omega)\, {\rm e}^{-{\rm i}\omega\tau}\, \frac{{\rm d}\omega}{2\pi}. \tag{III.10b}$$

[(42)] Here we implicitly assume that $\tilde{\chi}_{BA}(\omega)$ fulfills some integrability condition.

[(aj)] G. Green, 1793–1841 [(ak)] R. Kubo, 1920–1995

Remark: If the equilibrated system is subject to a sinusoidal force $f(t) = f_\omega \cos\omega t = \mathrm{Re}\big(f_\omega\, \mathrm{e}^{-\mathrm{i}\omega t}\big)$ with $f_\omega \in \mathbb{R}$, then its linear response (III.8) reads[(43)]

$$\big\langle \hat{B}_{\mathrm{I}}(t)\big\rangle_{\mathrm{n.eq.}} = \big\langle \hat{B}\,\big\rangle_{\mathrm{eq.}} + \mathrm{Re}\big(f_\omega \tilde{\chi}_{BA}(\omega)\mathrm{e}^{-\mathrm{i}\omega t}\big),$$

i.e. the response is also sinusoidal, although it will in general be out of phase with the exciting force, since $\tilde{\chi}_{BA}(\omega)$ is complex.

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

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.2.1 Calculation of the linear response function

We consider the quantum-mechanical system of § III.1.1, submitted to the small perturbation $\hat{W}(t) = -f(t)\hat{A}$ introduced in § III.1.2.

Let $\hat{\rho}_{\rm I}(t) \equiv {\rm e}^{{\rm i}\hat{H}_0 t/\hbar}\,\hat{\rho}\,{\rm e}^{-{\rm i}\hat{H}_0 t/\hbar}$ denote the interaction-picture representation of the density operator. Since the free evolution under the influence of $\hat{H}_0$ is accounted for by the transformation, the evolution in the presence of the perturbation (III.7) is governed by

$$\frac{{\rm d}\hat{\rho}_{\rm I}(t)}{{\rm d}t} = \frac{1}{{\rm i}\hbar}\big[\hat{W}_{\rm I}(t),\hat{\rho}_{\rm I}(t)\big], \quad \text{with} \quad \hat{W}_{\rm I}(t) = -f(t)\hat{A}_{\rm I}(t), \tag{III.24}$$

where $\hat{A}_{\rm I}(t)$ is defined according to Eq. (III.3). To first order in $f(t)$, the solution to this equation with the initial condition $\hat{\rho}_{\rm I}(-\infty) = \hat{\rho}_{\rm eq.}$ is

$$\hat{\rho}_{\rm I}(t) = \hat{\rho}_{\rm eq.} + \frac{\rm i}{\hbar}\int_{-\infty}^{t} f(t')\big[\hat{A}_{\rm I}(t'),\hat{\rho}_{\rm I}(t')\big]\,{\rm d}t' = \hat{\rho}_{\rm eq.} + \frac{\rm i}{\hbar}\int_{-\infty}^{t} f(t')\big[\hat{A}_{\rm I}(t'),\hat{\rho}_{\rm eq.}\big]\,{\rm d}t' + \mathcal{O}(f^2). \tag{III.25}$$

Multiplying with $\hat{B}_{\rm I}(t)$ and taking the trace, this leads to

$$\big\langle \hat{B}_{\rm I}(t)\big\rangle_{\rm n.eq.} = {\rm Tr}\big[\hat{B}_{\rm I}(t)\hat{\rho}_{\rm I}(t)\big] = \big\langle \hat{B}\,\big\rangle_{\rm eq.} + \frac{\rm i}{\hbar}\int_{-\infty}^{t} f(t')\,{\rm Tr}\big\{\hat{B}_{\rm I}(t)\big[\hat{A}_{\rm I}(t'),\hat{\rho}_{\rm eq.}\big]\big\}\,{\rm d}t' + \mathcal{O}(f^2).$$

Expanding explicitly the commutator and using the invariance of the trace under cyclic permutations, so as to isolate $\hat{\rho}_{\rm eq.}$, one finds that the trace in the integrand can be rewritten as

$${\rm Tr}\big\{\hat{B}_{\rm I}(t)\big[\hat{A}_{\rm I}(t'),\hat{\rho}_{\rm eq.}\big]\big\} = {\rm Tr}\big\{\hat{\rho}_{\rm eq.}\big[\hat{B}_{\rm I}(t),\hat{A}_{\rm I}(t')\big]\big\} = \Big\langle\big[\hat{B}_{\rm I}(t),\hat{A}_{\rm I}(t')\big]\Big\rangle_{\rm eq.} = \Big\langle\big[\hat{B}_{\rm I}(t-t'),\hat{A}_{\rm I}(0)\big]\Big\rangle_{\rm eq.},$$

where the last identity comes from inserting the terms ${\rm e}^{{\rm i}\hat{H}_0 t/\hbar}$, ${\rm e}^{{\rm i}\hat{H}_0 t'/\hbar}$ and their complex conjugates and invoking the invariance of the trace under cyclic permutations and the commutativity of $\hat{\rho}_{\rm eq.}$

and $\hat{H}_0$. In addition, one can insert a Heaviside[(al)] function $\Theta(t-t')$ in the integrand, so as to extend the upper bound of the integral to ∞.

All in all, this yields the *Kubo formula*

$$\left\langle \hat{B}_{\rm I}(t)\right\rangle_{\rm n.eq.} = \left\langle \hat{B}\,\right\rangle_{\rm eq.} + \int_{-\infty}^{\infty} \chi_{BA}(t-t')\, f(t')\, {\rm d}t' + \mathcal{O}(f^2), \qquad \text{(III.8)}$$

with χ_{BA} explicitly given as

$$\chi_{BA}(\tau) = \frac{\rm i}{\hbar}\left\langle \left[\hat{B}_{\rm I}(\tau), \hat{A}\right]\right\rangle_{\rm eq.} \Theta(\tau). \qquad \text{(III.26)}$$

As had already been anticipated, the retarded propagator (III.26), which characterizes the behavior of the system when it is driven out of equilibrium by an external perturbation, can actually be expressed in terms of a two-time average in the equilibrium state.

Remarks:

∗ When it can be performed, the computation of the interaction-picture representation of the operator conjugate to the perturbing force $f(t)$ allows one to derive the response function at once.

∗ The first identity in Eq. (III.25) embodies *Duhamel's*[(am)] *principle* for the solution of the linear differential equation (III.24), expressing it in terms of the initial condition (here at $t_0 = -\infty$) and the history between t_0 and t.

[(al)] O. Heaviside, 1850–1925 [(am)] J.-M. Duhamel, 1797–1872