3.2 Response functions

In this section, we shall deduce an expression for the response function $\phi_{BA}(t)$, in terms of the operators $\hat{B}$ and $\hat{A}$ and the unperturbed Hamiltonian $\mathcal{H}_0$. In the preceding section, we assumed implicitly the use of the Schrödinger picture. If instead we adopt the Heisenberg picture, the wave functions are independent of time, while the operators become time-dependent. In the Heisenberg picture, the operators are

$$\hat{B}(t) = e^{i\mathcal{H}t/\hbar}\,\hat{B}\,e^{-i\mathcal{H}t/\hbar}, \tag{3.2.1}$$

corresponding to the equation of motion

$$\frac{d}{dt}\hat{B}(t) = \frac{i}{\hbar}[\,\mathcal{H}\,,\,\hat{B}(t)\,] \tag{3.2.2}$$

(assuming that $\hat{B}$ does not depend explicitly on time). Because the wave functions are independent of time, in the Heisenberg picture, the corresponding density operator ρ_H must also be. Hence we may write (3.1.3)

$$\langle\hat{B}(t)\rangle = \mathrm{Tr}\big\{\rho(t)\,\hat{B}\big\} = \mathrm{Tr}\big\{\rho_H\,\hat{B}(t)\big\}. \tag{3.2.3}$$

Introducing (3.2.1) into this expression, and recalling that the trace is invariant under a cyclic permutation of the operators within it, we obtain

$$\rho(t) = e^{-i\mathcal{H}t/\hbar}\,\rho_H\,e^{i\mathcal{H}t/\hbar},$$

or

$$\frac{d}{dt}\rho(t) = -\frac{i}{\hbar}[\,\mathcal{H}\,,\,\rho(t)\,]. \tag{3.2.4}$$

The equation of motion derived for the density operator, in the Schrödinger picture, is similar to the Heisenberg equation of motion above, except for the change of sign in front of the commutator.

The density operator may be written as the sum of two terms:

$$\rho(t) = \rho_0 + \rho_1(t) \qquad \text{with} \quad [\,\mathcal{H}_0\,,\,\rho_0] = 0, \tag{3.2.5}$$

where ρ_0 is the density operator (3.1.1) of the thermal-equilibrium state which, by definition, must commute with $\mathcal{H}_0$, and the additional contribution due to $f(t)$ is assumed to vanish at $t \to -\infty$. In order to derive $\rho_1(t)$ to leading order in $f(t)$, we shall first consider the following density operator, in the *interaction picture*,

$$\rho_I(t) \equiv e^{i\mathcal{H}_0 t/\hbar}\,\rho(t)\,e^{-i\mathcal{H}_0 t/\hbar}, \tag{3.2.6}$$

for which

$$\begin{aligned}\frac{d}{dt}\rho_I(t) &= e^{i\mathcal{H}_0 t/\hbar}\left\{\frac{i}{\hbar}[\,\mathcal{H}_0\,,\,\rho(t)\,] + \frac{d}{dt}\rho(t)\right\}e^{-i\mathcal{H}_0 t/\hbar}\\ &= -\frac{i}{\hbar}e^{i\mathcal{H}_0 t/\hbar}\,[\,\mathcal{H}_1\,,\,\rho(t)\,]\,e^{-i\mathcal{H}_0 t/\hbar}.\end{aligned}$$

Because $\mathcal{H}_1$ is linear in $f(t)$, we may replace $\rho(t)$ by ρ_0 in calculating the linear response, giving

$$\frac{d}{dt}\rho_I(t) \simeq -\frac{i}{\hbar}\big[\,e^{i\mathcal{H}_0 t/\hbar}\,\mathcal{H}_1\,e^{-i\mathcal{H}_0 t/\hbar}\,,\,\rho_0\,\big] = \frac{i}{\hbar}[\,\hat{A}_0(t)\,,\,\rho_0\,]f(t),$$

using (3.2.5) and defining

$$\hat{A}_0(t) = e^{i\mathcal{H}_0 t/\hbar}\,\hat{A}\,e^{-i\mathcal{H}_0 t/\hbar}.$$

According to (3.2.6), taking into account the boundary condition, the time-dependent density operator is

$$\begin{aligned}\rho(t) &= e^{-i\mathcal{H}_0 t/\hbar}\Big(\int_{-\infty}^{t}\frac{d}{dt'}\rho_I(t')dt' + \rho_0\Big)e^{i\mathcal{H}_0 t/\hbar}\\ &= \rho_0 + \frac{i}{\hbar}\int_{-\infty}^{t}[\,\hat{A}_0(t'-t)\,,\,\rho_0\,]\,f(t')dt',\end{aligned} \tag{3.2.7}$$

to first order in the external perturbations. This determines the time dependence of, for example, $\hat{B}$ as

$$\begin{aligned}\langle\hat{B}(t)\rangle - \langle\hat{B}\rangle &= \mathrm{Tr}\big\{\,(\rho(t)-\rho_0)\;\hat{B}\big\}\\ &= \frac{i}{\hbar}\,\mathrm{Tr}\Big\{\int_{-\infty}^{t}[\,\hat{A}_0(t'-t)\,,\,\rho_0\,]\,\hat{B}\,f(t')dt'\Big\}\end{aligned}$$

and, utilizing the invariance of the trace under cyclic permutations, we obtain, to leading order,

$$\begin{aligned}\langle\hat{B}(t)\rangle - \langle\hat{B}\rangle &= \frac{i}{\hbar}\int_{-\infty}^{t}\mathrm{Tr}\big\{\rho_0\,[\,\hat{B}\,,\,\hat{A}_0(t'-t)\,]\big\}\,f(t')dt'\\ &= \frac{i}{\hbar}\int_{-\infty}^{t}\langle\,[\,\hat{B}_0(t)\,,\,\hat{A}_0(t')\,]\,\rangle_0\,f(t')dt'.\end{aligned} \tag{3.2.8}$$

A comparison of this result with the definition (3.1.4) of the response function then gives

$$\phi_{BA}(t-t') = \frac{i}{\hbar}\theta(t-t')\langle\,[\,\hat{B}(t)\,,\,\hat{A}(t')\,]\,\rangle, \tag{3.2.9}$$

where the unit step function, $\theta(t) = 0$ or 1 when $t < 0$ or $t > 0$ respectively, is introduced in order to ensure that ϕ_{BA} satisfies the causality principle (3.1.5). In this final result, and below, we suppress the index 0, but we stress that both the variations with time and the ensemble average are thermal-equilibrium values determined by $\mathcal{H}_0$, and are unaffected by the external disturbances. This expression in terms of microscopic quantities, is called *the Kubo formula* for the response function (Kubo 1957, 1966).

The expression (3.2.9) is the starting point for introducing a number of useful functions:

$$K_{BA}(t) = \frac{i}{\hbar}\langle\,[\hat{B}(t)\,,\,\hat{A}\,]\,\rangle = \frac{i}{\hbar}\langle\,[\hat{B}\,,\,\hat{A}(-t)\,]\,\rangle \tag{3.2.10}$$

is also called a response function. $\hat{A}$ is a shorthand notation for $\hat{A}(t=0)$. The inverse response function $K_{AB}(t)$, which determines $\langle\hat{A}(t)\rangle$ caused by the perturbation $\mathcal{H}_1 = -f(t)\hat{B}$, is

$$K_{AB}(t) = \frac{i}{\hbar}\langle\,[\hat{A}(t)\,,\,\hat{B}\,]\,\rangle = -K_{BA}(-t),$$

and $K_{BA}(t)$ can be expressed in terms of the corresponding causal response functions as

$$K_{BA}(t) = \begin{cases} \phi_{BA}(t) & \text{for} \quad t > 0 \\ -\phi_{AB}(-t) & \text{for} \quad t < 0. \end{cases}$$

The susceptibility is divided into two terms, the reactive part

$$\chi'_{BA}(z) = \chi'_{AB}(-z^*) \equiv \frac{1}{2}\big\{\chi_{BA}(z) + \chi_{AB}(-z^*)\big\}, \tag{3.2.11a}$$

and the absorptive part

$$\chi''_{BA}(z) = -\chi''_{AB}(-z^*) \equiv \frac{1}{2i}\big\{\chi_{BA}(z) - \chi_{AB}(-z^*)\big\}, \tag{3.2.11b}$$

so that

$$\chi_{BA}(z) = \chi'_{BA}(z) + i\chi''_{BA}(z) \tag{3.2.11c}$$

and, according to the Kramers–Kronig relation (3.1.10),

$$\chi'_{BA}(\omega) = \frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{\chi''_{BA}(\omega')}{\omega'-\omega}d\omega' \quad ; \quad \chi''_{BA}(\omega) = -\frac{1}{\pi}\mathcal{P}\int_{-\infty}^{\infty}\frac{\chi'_{BA}(\omega')}{\omega'-\omega}d\omega'. \tag{3.2.11d}$$

In these equations, $\chi_{AB}(-\omega)$ is the boundary value obtained by taking $z = \omega + i\epsilon$, i.e. as $\lim_{\epsilon\to 0^+}\chi_{AB}(-z^* = -\omega + i\epsilon)$, corresponding to the condition that $\chi_{AB}(-z^*)$, like $\chi_{AB}(z)$, is analytic in the upper half-plane. The appropriate Laplace transform of $K_{BA}(t)$ with this property is

$$\begin{aligned} K_{BA}(z) &= \int_{-\infty}^{\infty} K_{BA}(t)\, e^{i(z_1 t + i z_2|t|)} dt \\ &= \int_0^{\infty}\phi_{BA}(t)\, e^{izt} dt - \int_0^{\infty}\phi_{AB}(t)\, e^{-iz^* t} dt. \end{aligned}$$

Hence

$$K_{BA}(z) = 2i\,\chi''_{BA}(z). \tag{3.2.12}$$

Next we introduce the dynamic *correlation function*, sometimes referred to as the *scattering function*. It is defined as follows:

$$S_{BA}(t) \equiv \langle\hat{B}(t)\,\hat{A}\rangle - \langle\hat{B}\rangle\langle\hat{A}\rangle = \langle\hat{B}\,\hat{A}(-t)\rangle - \langle\hat{B}\rangle\langle\hat{A}\rangle, \tag{3.2.13}$$

and is related to the response function introduced earlier by

$$K_{BA}(t) = \frac{i}{\hbar}\{S_{BA}(t) - S_{AB}(-t)\}. \qquad (3.2.14)$$

The different response functions obey a number of symmetry relations, due to the invariance of the trace under a cyclic permutation of the operators. To derive the first, we recall that the Hermitian conjugate of an operator is defined by

$$(< \alpha | \hat{B} | \alpha' >)^* = < \alpha' | \hat{B}^\dagger | \alpha > .$$

If we assume that a certain set of state vectors $|\alpha >$ constitutes a diagonal representation, i.e. $\mathcal{H}_0 |\alpha > = E_\alpha |\alpha >$, then it is straightforward to show that

$$\langle \hat{B}(t)\, \hat{A} \rangle^* = \langle \hat{A}^\dagger(-t)\, \hat{B}^\dagger \rangle,$$

leading to the symmetry relations

$$K^*_{BA}(t) = K_{B^\dagger A^\dagger}(t)$$

and

$$\chi^*_{BA}(z) = \chi_{B^\dagger A^\dagger}(-z^*). \qquad (3.2.15)$$

Another important relation is derived as follows:

$$\begin{aligned}\langle \hat{B}(t)\, \hat{A} \rangle &= \frac{1}{Z}\mathrm{Tr}\left\{ e^{-\beta\mathcal{H}_0}\, e^{i\mathcal{H}_0 t/\hbar}\, \hat{B}\, e^{-i\mathcal{H}_0 t/\hbar}\, \hat{A} \right\} \\ &= \frac{1}{Z}\mathrm{Tr}\left\{ e^{i\mathcal{H}_0 (t+i\beta\hbar)/\hbar}\, \hat{B}\, e^{-i\mathcal{H}_0 (t+i\beta\hbar)/\hbar}\, e^{-\beta\mathcal{H}_0}\, \hat{A} \right\} \\ &= \frac{1}{Z}\mathrm{Tr}\left\{ e^{-\beta\mathcal{H}_0}\, \hat{A}\, \hat{B}(t+i\beta\hbar) \right\} = \langle \hat{A}\, \hat{B}(t+i\beta\hbar) \rangle,\end{aligned}$$

implying that

$$S_{BA}(t) = S_{AB}(-t - i\beta\hbar). \qquad (3.2.16)$$

In any realistic system which, rather than being isolated, is in contact with a thermal bath at temperature T, the correlation function $S_{BA}(t)$ vanishes in the limits $t \to \pm\infty$, corresponding to the condition $\langle \hat{B}(t = \pm\infty)\, \hat{A} \rangle = \langle \hat{B} \rangle \langle \hat{A} \rangle$. If we further assume that $S_{BA}(t)$ is an analytic function in the interval $|t_2| \leq \beta$ of the complex t-plane, then the Fourier transform of (3.2.16) is

$$S_{BA}(\omega) = e^{\beta\hbar\omega}\, S_{AB}(-\omega), \qquad (3.2.17)$$

which is usually referred to as being the *condition of detailed balance.* Combining this condition with the expressions (3.2.12) and (3.2.14), we get the following important relation between the correlation function and the susceptibility:

$$S_{BA}(\omega) = 2\hbar \frac{1}{1 - e^{-\beta\hbar\omega}} \chi''_{BA}(\omega), \tag{3.2.18}$$

which is called the *fluctuation–dissipation theorem*. This relation expresses explicitly the close connection between the spontaneous fluctuations in the system, as described by the correlation function, and the response of the system to external perturbations, as determined by the susceptibility.

The calculations above do not depend on the starting assumption that $\hat{B}$ (or $\hat{A}$) is a physical observable, i.e. that $\hat{B}$ should be equal to $\hat{B}^\dagger$. This has the advantage that, if the Kubo formula (3.2.9) is taken to be the starting point instead of eqn (3.1.4), the formalism applies more generally.