3.3 Energy absorption and the Green function

In this section, we first present a calculation of the energy transferred to the system by the external perturbation $\mathcal{H}_1 = -\hat{A}\, f(t)$ in (3.1.2), incidentally justifying the names of the two susceptibility components in (3.2.11). The energy absorption can be expressed in terms of $\chi_{AA}(\omega)$ and, without loss of generality, $\hat{A}$ may here be assumed to be a Hermitian operator, so that $\hat{A} = \hat{A}^\dagger$. In this case, $f(t)$ is real, and considering a harmonic variation

$$f(t) = f_0 \cos(\omega_0 t) = \tfrac{1}{2} f_0 \left(e^{i\omega_0 t} + e^{-i\omega_0 t} \right) \quad \text{with} \quad f_0^* = f_0,$$

then

$$f(\omega) = \pi f_0 \{\delta(\omega-\omega_0)+\delta(\omega+\omega_0)\}, \quad \text{as} \quad \int_{-\infty}^{\infty} e^{i(\omega-\omega_0)t} dt = 2\pi\delta(\omega-\omega_0),$$

and we have

$$\langle \hat{A}(t) \rangle - \langle \hat{A} \rangle = \tfrac{1}{2} f_0 \left\{ \chi_{AA}(-\omega_0)\, e^{i\omega_0 t} + \chi_{AA}(\omega_0)\, e^{-i\omega_0 t} \right\}.$$

The introduction of $\hat{A} = \hat{B} = \hat{A}^\dagger$ in (3.2.15), and in the definition (3.2.11), yields

$$\begin{aligned} \chi'_{AA}(\omega)^* &= \chi'_{AA}(\omega) = \chi'_{AA}(-\omega) \\ \chi''_{AA}(\omega)^* &= \chi''_{AA}(\omega) = -\chi''_{AA}(-\omega), \end{aligned} \tag{3.3.1}$$

and these symmetry relations allow us to write

$$\langle \hat{A}(t) \rangle - \langle \hat{A} \rangle = f_0 \left\{ \chi'_{AA}(\omega_0) \cos(\omega_0 t) + \chi''_{AA}(\omega_0) \sin(\omega_0 t) \right\}.$$

The part of the response which is in phase with the external force is proportional to $\chi'_{AA}(\omega_0)$, which is therefore called the reactive component. The rate of energy absorption due to the field is

$$Q = \frac{d}{dt}\langle \mathcal{H} \rangle = \langle \partial \mathcal{H}/\partial t \rangle = -\langle \hat{A}(t) \rangle \, \partial f/\partial t,$$

which shows that the *mean* dissipation rate is determined by the out-of-phase response proportional to $\chi''_{AA}(\omega)$:

$$\overline{Q} = \tfrac{1}{2} f_0^2 \, \omega_0 \, \chi''_{AA}(\omega_0) \tag{3.3.2}$$

and $\chi''_{AA}(\omega)$ is therefore called the absorptive part of the susceptibility.

If the eigenvalues E_α and the corresponding eigenstates $|\alpha>$ for the Hamiltonian $\mathcal{H}(=\mathcal{H}_0)$ are known, it is possible to derive an explicit expression for $\chi_{BA}(\omega)$. According to the definition (3.2.10),

$$\begin{aligned} K_{BA}(t) = \frac{i}{\hbar}\frac{1}{Z}\mathrm{Tr}\Big\{ e^{-\beta\mathcal{H}} \left[e^{i\mathcal{H}t/\hbar} \, \hat{B} \, e^{-i\mathcal{H}t/\hbar} \, , \, \hat{A} \right] \Big\} = \\ \frac{i}{\hbar}\frac{1}{Z}\sum_{\alpha\alpha'} e^{-\beta E_\alpha} \left\{ e^{iE_\alpha t/\hbar} < \alpha | \hat{B} | \alpha' > e^{-iE_{\alpha'} t/\hbar} < \alpha' | \hat{A} | \alpha > \right. \\ \left. - < \alpha | \hat{A} | \alpha' > e^{iE_{\alpha'} t/\hbar} < \alpha' | \hat{B} | \alpha > e^{-iE_\alpha t/\hbar} \right\}. \end{aligned}$$

Interchanging α and α' in the last term, and introducing the population factor

$$n_\alpha = \frac{1}{Z} e^{-\beta E_\alpha} \quad ; \quad Z = \sum_{\alpha'} e^{-\beta E_{\alpha'}}, \tag{3.3.3a}$$

we get

$$K_{BA}(t) = \frac{i}{\hbar} \sum_{\alpha\alpha'} < \alpha | \hat{B} | \alpha' >< \alpha' | \hat{A} | \alpha > (n_\alpha - n_{\alpha'}) \, e^{i(E_\alpha - E_{\alpha'})t/\hbar}, \tag{3.3.3b}$$

and hence

$$\begin{aligned} \chi_{BA}(\omega) &= \lim_{\epsilon \to 0^+} \int_0^\infty K_{BA}(t) \, e^{i(w+i\epsilon)t} dt \\ &= \lim_{\epsilon \to 0^+} \sum_{\alpha\alpha'} \frac{< \alpha | \hat{B} | \alpha' >< \alpha' | \hat{A} | \alpha >}{E_{\alpha'} - E_\alpha - \hbar\omega - i\hbar\epsilon} (n_\alpha - n_{\alpha'}), \end{aligned} \tag{3.3.4a}$$

or equivalently

$$\begin{aligned}\chi_{AB}(-\omega) &= \lim_{\epsilon\to 0^+} \chi_{AB}(-\omega + i\epsilon) \\ &= \lim_{\epsilon\to 0^+} \sum_{\alpha\alpha'} \frac{<\alpha|\hat{A}|\alpha'><\alpha'|\hat{B}|\alpha>}{E_{\alpha'} - E_\alpha + \hbar\omega - i\hbar\epsilon}(n_\alpha - n_{\alpha'}).\end{aligned} \tag{3.3.4b}$$

An interchange of α and α' shows this expression to be the same as (3.3.4a), with ϵ replaced by $-\epsilon$. The application of Dirac's formula then yields the absorptive part of the susceptibility (3.2.11b) as

$$\chi''_{BA}(\omega) = \pi \sum_{\alpha\alpha'} <\alpha|\hat{B}|\alpha'><\alpha'|\hat{A}|\alpha>(n_\alpha - n_{\alpha'})\,\delta\big(\hbar\omega - (E_{\alpha'} - E_\alpha)\big) \tag{3.3.5}$$

(equal to $K_{BA}(\omega)/2i$ in accordance with (3.2.12)), whereas the reactive part (3.2.11a) is

$$\chi'_{BA}(\omega) = \sum_{\alpha\alpha'}^{E_\alpha\neq E_{\alpha'}} \frac{<\alpha|\hat{B}|\alpha'><\alpha'|\hat{A}|\alpha>}{E_{\alpha'} - E_\alpha - \hbar\omega}(n_\alpha - n_{\alpha'}) + \chi'_{BA}(el)\,\delta_{\omega 0}, \tag{3.3.6a}$$

where

$$\delta_{\omega 0} \equiv \lim_{\epsilon\to 0^+} \frac{i\epsilon}{\omega + i\epsilon} = \begin{cases} 1 & \text{if} \quad \omega = 0 \\ 0 & \text{if} \quad \omega \neq 0, \end{cases}$$

and the elastic term $\chi'_{BA}(el)$, which only contributes in the static limit $\omega = 0$, is

$$\chi'_{BA}(el) = \beta\Big\{ \sum_{\alpha\alpha'}^{E_\alpha = E_{\alpha'}} <\alpha|\hat{B}|\alpha'><\alpha'|\hat{A}|\alpha> n_\alpha \; - \; \langle\hat{B}\rangle\langle\hat{A}\rangle \Big\}. \tag{3.3.6b}$$

We remark that $\chi'_{BA}(\omega)$ and $\chi''_{BA}(\omega)$ are often referred to respectively as the real and the imaginary part of $\chi_{BA}(\omega)$. This terminology is not valid in general, but only if the matrix-element products are real, as they are if, for instance, $\hat{B} = \hat{A}^\dagger$. The presence of the elastic term in the reactive response requires some additional consideration. There are no elastic contributions to $K_{BA}(t)$, nor hence to $\chi''_{BA}(\omega)$, because $n_\alpha - n_{\alpha'} \equiv 0$ if $E_\alpha = E_{\alpha'}$. Nevertheless, the appearance of an extra contribution at $\omega = 0$, not obtainable directly from $K_{BA}(t)$, is possible because the energy denominator in (3.3.4) vanishes in the limit $|\omega + i\epsilon| \to 0$, when $E_\alpha = E_{\alpha'}$. In order to derive this contribution, we consider the equal-time correlation function

$$\begin{aligned}S_{BA}(t=0) &= \langle(\hat{B} - \langle\hat{B}\rangle)(\hat{A} - \langle\hat{A}\rangle)\rangle \\ &= \sum_{\alpha\alpha'} <\alpha|\hat{B}|\alpha'><\alpha'|\hat{A}|\alpha> n_\alpha \; - \; \langle\hat{B}\rangle\langle\hat{A}\rangle\end{aligned} \tag{3.3.7a}$$

which, according to the fluctuation–dissipation theorem (3.2.18), should be

$$S_{BA}(t=0) = \frac{1}{2\pi}\int_{-\infty}^{\infty} S_{BA}(\omega)\,d\omega = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{1}{1-e^{-\beta\hbar\omega}}\,\chi''_{BA}(\omega)d(\hbar\omega). \tag{3.3.7b}$$

Introducing (3.3.5), the integration is straightforward, except in a narrow interval around $\omega = 0$, and we obtain

$$S_{BA}(t=0) = \sum_{\alpha\alpha'}^{E_\alpha\neq E_{\alpha'}} <\alpha\,|\hat{B}\,|\alpha'><\alpha'\,|\hat{A}\,|\alpha> n_\alpha + \lim_{\gamma\to 0^+}\int_{-\gamma}^{\gamma}\frac{\chi''_{BA}(\omega)}{\pi\beta\omega}d\omega$$

after replacing $1-e^{-\beta\hbar\omega}$ with $\beta\hbar\omega$ in the limit $\omega\to 0$. A comparison of this expression for $S_{BA}(t=0)$ with (3.3.7a) shows that the last integral has a definite value:

$$\lim_{\gamma\to 0^+}\int_{-\gamma}^{\gamma}\frac{\chi''_{BA}(\omega)}{\pi\beta\omega}d\omega = \sum_{\alpha\alpha'}^{E_\alpha=E_{\alpha'}} <\alpha\,|\hat{B}\,|\alpha'><\alpha'\,|\hat{A}\,|\alpha> n_\alpha \,-\, \langle\hat{B}\rangle\langle\hat{A}\rangle. \tag{3.3.8}$$

The use of the Kramers–Kronig relation (3.1.10), in the form of (3.2.11d), for calculating $\chi'_{BA}(0)$ then gives rise to the extra contribution

$$\chi'_{BA}(el) = \lim_{\gamma\to 0^+}\frac{1}{\pi}\int_{-\gamma}^{\gamma}\frac{\chi''_{BA}(\omega)}{\omega}d\omega \tag{3.3.9}$$

to the reactive susceptibility at zero frequency, as anticipated in (3.3.6b). The zero-frequency result, $\chi_{BA}(0) = \chi'_{BA}(0)$, as given by (3.3.6), is the same as the conventional isothermal susceptibility (2.1.18) for the magnetic moments, where the elastic and inelastic contributions are respectively the Curie and the Van Vleck terms. This elastic contribution is discussed in more detail by, for instance, Suzuki (1971).

The results (3.3.4–6) show that, if the eigenstates of the Hamiltonian are discrete and the matrix-elements of the operators $\hat{B}$ and $\hat{A}$ between these states are well-defined, the poles of $\chi_{BA}(z)$ all lie on the real axis. This has the consequence that the absorptive part $\chi''_{BA}(\omega)$ (3.3.5) becomes a sum of δ-functions, which are only non-zero when $\hbar\omega$ is equal to the *excitation* energies $E_{\alpha'} - E_\alpha$. In such a system, no spontaneous transitions occur. In a real macroscopic system, the distribution of states is continuous, and only the ground state may be considered as a well-defined discrete state. At non-zero temperatures, the parameters of the system are subject to fluctuations in space and time. The introduction of a non-zero probability for a spontaneous transition between the 'levels' α and α' can be included in a phenomenological way by replacing the energy difference $E_{\alpha'} - E_\alpha$ in (3.3.4) by $(E_{\alpha'} - E_\alpha) - i\,\Gamma_{\alpha'\alpha}(\omega)$, where the parameters, including the energy difference, usually depend on ω. According to the general stability and causality requirements, the poles of $\chi_{BA}(z)$ at $z = z_{\alpha'\alpha} = (E_{\alpha'} - E_\alpha) - i\,\Gamma_{\alpha'\alpha}$ must lie in the lower half-plane, implying that $\Gamma_{\alpha'\alpha}$ has to be positive (or zero). In the case where $|E_{\alpha'} - E_\alpha| \gg \Gamma_{\alpha'\alpha}$, the ω-dependence of these parameters is unimportant, and the δ-function in (3.3.5) is effectively replaced by a *Lorentzian*:

$$\begin{aligned}\chi''_{BA}(\omega) \simeq \sum_{\alpha\alpha'} \frac{<\alpha|\hat{B}|\alpha'><\alpha'|\hat{A}|\alpha>}{(E_{\alpha'} - E_\alpha - \hbar\omega)^2 + \Gamma^2_{\alpha'\alpha}}\, \Gamma_{\alpha'\alpha}(n_\alpha - n_{\alpha'}) \\ + \frac{\hbar\omega\Gamma_0}{(\hbar\omega)^2 + \Gamma_0^2}\, \chi'_{BA}(el),\end{aligned} \tag{3.3.10}$$

with a *linewidth*, or more precisely FWHM (full width at half maximum), of $2\Gamma_{\alpha'\alpha}$. In (3.3.10), we have added the *quasi-elastic* response due to a pole at $z = -i\,\Gamma_0$, which replaces the one at $z = 0$. The corresponding reactive part of the susceptibility is

$$\begin{aligned}\chi'_{BA}(\omega) \simeq \sum_{\alpha\alpha'} \frac{<\alpha|\hat{B}|\alpha'><\alpha'|\hat{A}|\alpha>}{(E_{\alpha'} - E_\alpha - \hbar\omega)^2 + \Gamma^2_{\alpha'\alpha}} (E_{\alpha'} - E_\alpha - \hbar\omega)(n_\alpha - n_{\alpha'}) \\ + \frac{\Gamma_0^2}{(\hbar\omega)^2 + \Gamma_0^2}\, \chi'_{BA}(el).\end{aligned} \tag{3.3.11}$$

The non-zero linewidth corresponds to an exponential decay of the oscillations in the time dependence of, for instance, the correlation function:

$$S_{BA}(t) \,\sim\, e^{-iz_{\alpha'\alpha}t/\hbar} = e^{-i(E_{\alpha'} - E_\alpha)t/\hbar}\, e^{-\Gamma_{\alpha'\alpha}t/\hbar}.$$

The absorption observed in a *resonance* experiment is proportional to $\chi''_{AA}(\omega)$. A peak in the absorption spectrum is interpreted as an *elementary* or *quasi-particle excitation*, or as a *normal mode* of the dynamic variable $\hat{A}$, with a *lifetime* $\tau = \hbar/\Gamma_{\alpha'\alpha}$. A pole at $z = -i\Gamma_0$ is said to represent a *diffusive mode*. Such a pole is of particular importance for those transport coefficients determined by the low-frequency or hydrodynamic properties of the system. Kubo (1957, 1966) gives a detailed discussion of this subject. As we shall see later, the differential scattering cross-section of, for example, neutrons in the Born-approximation is proportional to a correlation function, and hence to $\chi''(\omega)$. This implies that the presence of elementary excitations in the system leads to peaks in the intensity of scattered neutrons as a function of the energy transfer. Finally, the dynamic correlation-functions are related directly to various thermodynamic second-derivatives, such as the compressibility and the magnetic susceptibility, and thereby indirectly to the corresponding first-derivatives, like the specific heat and the magnetization. Consequently, most physical properties of a macroscopic system near equilibrium may be described in terms of the correlation functions.

As a supplement to the response function $\phi_{BA}(t-t')$, we now introduce the *Green function*, defined as

$$\begin{aligned} G_{BA}(t-t') &\equiv \langle\langle \hat{B}(t)\,;\,\hat{A}(t')\rangle\rangle \\ &\equiv -\frac{i}{\hbar}\theta(t-t')\langle\,[\,\hat{B}(t)\,,\,\hat{A}(t')\,]\,\rangle = -\phi_{BA}(t-t'). \end{aligned} \tag{3.3.12}$$

This Green function is often referred to as the *double-time* or the *retarded* Green function (Zubarev 1960), and it is simply our previous response function, but with the opposite sign. Introducing the Laplace transform $G_{BA}(z)$ according to (3.1.7), we find, as before, that the corresponding Fourier transform is

$$\begin{aligned} G_{BA}(\omega) \equiv \langle\langle \hat{B}\,;\,\hat{A}\rangle\rangle_\omega &= \lim_{\epsilon\to 0^+} G_{BA}(z=\omega+i\epsilon) \\ &= \lim_{\epsilon\to 0^+}\int_{-\infty(0)}^{\infty} G_{BA}(t)\,e^{i(\omega+i\epsilon)t}dt = -\chi_{BA}(\omega). \end{aligned} \tag{3.3.13}$$

We note that, if $\hat{A}$ and $\hat{B}$ are dimensionless operators, then $G_{BA}(\omega)$ or $\chi_{BA}(\omega)$ have the dimensions of inverse energy.

If $t'=0$, the derivative of the Green function with respect to t is

$$\begin{aligned} \frac{d}{dt}G_{BA}(t) &= -\frac{i}{\hbar}\Big(\delta(t)\langle\,[\,\hat{B}(t)\,,\,\hat{A}\,]\,\rangle + \theta(t)\langle\,[\,d\hat{B}(t)/dt\,,\,\hat{A}\,]\,\rangle\Big) \\ &= -\frac{i}{\hbar}\Big(\delta(t)\langle\,[\,\hat{B}\,,\,\hat{A}\,]\,\rangle - \frac{i}{\hbar}\theta(t)\langle\,[\,[\,\hat{B}(t)\,,\,\mathcal{H}\,]\,,\,\hat{A}\,]\,\rangle\Big). \end{aligned}$$

A Fourier transformation of this expression then leads to the *equation of motion* for the Green function:

$$\hbar\omega\langle\langle \hat{B}\,;\,\hat{A}\rangle\rangle_\omega - \langle\langle\,[\,\hat{B}\,,\,\mathcal{H}\,]\,;\,\hat{A}\rangle\rangle_\omega = \langle\,[\,\hat{B}\,,\,\hat{A}\,]\,\rangle. \tag{3.3.14a}$$

The suffix ω indicates the Fourier transforms (3.3.13), and $\hbar\omega$ is shorthand for $\hbar(\omega+i\epsilon)$ with $\epsilon\to 0^+$. In many applications, $\hat{A}$ and $\hat{B}$ are the same (Hermitian) operator, in which case the r.h.s. of (3.3.14*a*) vanishes and one may proceed to the second derivative. With the condition that $\langle\,[\,[\,[\,\hat{A}(t)\,,\,\mathcal{H}\,]\,,\,\mathcal{H}\,]\,,\,\hat{A}\,]\,\rangle$ is $-\langle\,[\,[\,\hat{A}(t)\,,\,\mathcal{H}\,]\,,\,[\,\hat{A}\,,\,\mathcal{H}\,]\,]\,\rangle$, the equation of motion for the Green function $\langle\langle\,[\,\hat{A}\,,\,\mathcal{H}\,]\,;\,\hat{A}\rangle\rangle_\omega$ leads to

$$(\hbar\omega)^2\langle\langle \hat{A}\,;\,\hat{A}\rangle\rangle_\omega + \langle\langle\,[\,\hat{A}\,,\,\mathcal{H}\,]\,;\,[\,\hat{A}\,,\,\mathcal{H}\,]\,\rangle\rangle_\omega = \langle\,[\,[\,\hat{A}\,,\mathcal{H}\,]\,,\,\hat{A}\,]\,\rangle. \tag{3.3.14b}$$

The pair of equations (3.3.14) will be the starting point for our application of linear response theory.

According to the definition (3.2.10) of $K_{BA}(t)$, and eqn (3.2.12),

$$K_{BA}(\omega) = 2i\chi''_{BA}(\omega) = -2iG''_{BA}(\omega).$$

We may write

$$\frac{i}{\pi}\int_{-\infty}^{\infty} \chi''_{BA}(\omega)\, e^{-i\omega t} d\omega = \frac{i}{\hbar}\langle\, [\, \hat{B}(t)\, ,\, \hat{A}\,]\, \rangle \tag{3.3.15}$$

and, setting $t = 0$, we obtain the following *sum rule*:

$$\frac{\hbar}{\pi}\int_{-\infty}^{\infty} \chi''_{BA}(\omega) d\omega = \langle\, [\, \hat{B}\, ,\, \hat{A}\,]\, \rangle, \tag{3.3.16}$$

which may be compared with the value obtained for the equal-time correlation function $\langle \hat{B}\,\hat{A}\rangle - \langle \hat{B}\rangle\langle \hat{A}\rangle$, (3.3.7). The Green function in (3.3.14a) must satisfy this sum rule, and we note that the thermal averages in (3.3.14a) and (3.3.16) are the same. Equation (3.3.16) is only the first of a whole series of sum rules.

The nth time-derivative of $\hat{B}(t)$ may be written

$$\frac{d^n}{dt^n}\hat{B}(t) = \left(\frac{i}{\hbar}\right)^n \mathcal{L}^n \hat{B}(t) \qquad \text{with} \quad \mathcal{L}\hat{B}(t) \equiv [\, \mathcal{H}\, ,\, \hat{B}(t)\,].$$

Taking the nth derivative on both sides of eqn (3.3.15), we get

$$\frac{i}{\pi}\int_{-\infty}^{\infty} (-i\omega)^n \chi''_{BA}(\omega)\, e^{-i\omega t} d\omega = \left(\frac{i}{\hbar}\right)^{n+1} \langle\, [\, \mathcal{L}^n \hat{B}(t)\, ,\, \hat{A}\,]\, \rangle.$$

Next we introduce the normalized *spectral weight function*

$$F_{BA}(\omega) = \frac{1}{\chi'_{BA}(0)}\frac{1}{\pi}\frac{\chi''_{BA}(\omega)}{\omega}, \quad \text{where} \quad \int_{-\infty}^{\infty} F_{BA}(\omega) d\omega = 1. \tag{3.3.17a}$$

The normalization of $F_{BA}(\omega)$ is a simple consequence of the Kramers–Kronig relation (3.2.11d). The nth order moment of ω, with respect to the spectral weight function $F_{BA}(\omega)$, is then defined as

$$\langle\, \omega^n \rangle_{BA} = \int_{-\infty}^{\infty} \omega^n F_{BA}(\omega) d\omega, \tag{3.3.17b}$$

which allows the relation between the nth derivatives at $t = 0$ to be written

$$\chi'_{BA}(0)\, \langle (\hbar\omega)^{n+1} \rangle_{BA} = (-1)^n \langle\, [\, \mathcal{L}^n \hat{B}\, ,\, \hat{A}\,]\, \rangle. \tag{3.3.18a}$$

These are the sum rules relating the spectral frequency-moments with the thermal expectation-values of operators obtainable from $\hat{B}$, $\hat{A}$, and $\mathcal{H}$. If $\hat{B} = \hat{A} = \hat{A}^{\dagger}$, then (3.3.1) shows that$F_{BA}(\omega)$ is even in ω, and all the odd moments vanish. In this case, the even moments are

$$\chi'_{AA}(0)\,\langle(\hbar\omega)^{2n}\rangle_{AA} = -\langle\,[\,\mathcal{L}^{2n-1}\hat{A}\,,\,\hat{A}\,]\,\rangle. \qquad (3.3.18b)$$