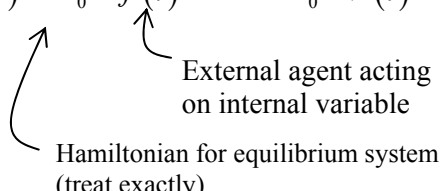


QUANTUM LINEAR RESPONSE FUNCTION

Let's treat the problem of the response of a system to an applied external force. Again,

$$H(t) = H_0 - f(t)A = H_0 + V(t)$$



If $V(t)$ represents a small change, we can treat this with perturbation theory in the interaction picture. Now A is an operator. We want to describe $\overline{A(t)}$ which we will get by ensemble averaging the expectation value of $A(t)$. Remember the expectation value for a single wavefunction is

$$\begin{aligned} \langle A(t) \rangle &= \langle \psi(t) | A | \psi(t) \rangle = \langle \psi | U^\dagger(t, t_0) A U(t, t_0) | \psi \rangle \\ &= \langle \psi | U_I^\dagger A_I U_I | \psi \rangle \end{aligned}$$

Where the propagation in the interaction picture is

$$U_I(t, t_0) = 1 + \frac{-i}{\hbar} \int_{t_0}^t V_I(\tau) U_I(\tau, t_0) d\tau \quad (\text{exact})$$

For the linear response we use the first order solution:

$$\begin{aligned} V_I(\tau) &= U_0^\dagger(\tau) V(\tau) U_0(\tau) \\ &= -f(\tau) U_0^\dagger(\tau) A U_0(\tau) \\ &= -f(\tau) A_I \end{aligned}$$

$$U_I(t, t_0) = 1 + \frac{i}{\hbar} \int_{t_0}^t d\tau f(\tau) A_I(\tau)$$

So, we can now calculate the value of the operator A at time t

$$\begin{aligned}
 A(t) &= U_I^\dagger A_I U_I \\
 &= \left\{ 1 - \frac{i}{\hbar} \int_{t_0}^t dt' f(t') A_I(t') \right\} A_I(t) \left\{ 1 + \frac{i}{\hbar} \int_{t_0}^t dt' f(t') A_I(t') \right\} \\
 &\cong A_I(t) + \frac{i}{\hbar} \int_{t_0}^t dt' f(t') \{ A_I(t) A_I(t') - A_I(t') A_I(t) \} \quad \text{retaining linear terms} \\
 &= A_I(t) + \frac{i}{\hbar} \int_{t_0}^t dt' f(t') [A_I(t), A_I(t')]
 \end{aligned}$$

Now, using $A_I(t) = U_0^\dagger(t) A U_0(t)$ and setting $t_0 = 0$ we can write

$$\begin{aligned}
 A(t) &= A_I(t) + \frac{i}{\hbar} \int_0^t dt' f(t') [A_I(t-t'), A_I(0)] \\
 &= A_I(t) + \frac{i}{\hbar} \int_0^\infty d\tau f(t-\tau) [A_I(\tau), A_I(0)] \quad \text{where } \tau = t - t'
 \end{aligned}$$

Now, what we want is the expectation value of A , that is $\langle \psi | A | \psi \rangle$, averaged over the ensemble, which we will write $\overline{\langle A(t) \rangle}$ for the moment. Taking into account that the force is applied equally to each member of ensemble we have

$$\overline{\langle A(t) \rangle} = \langle A \rangle + \frac{i}{\hbar} \int_0^\infty d\tau f(t-\tau) \langle \langle [A_I(\tau), A_I(0)] \rangle \rangle$$

The first term is independent of f , and so it comes from an equilibrium ensemble average

$$\langle \langle A_I \rangle \rangle = \sum_n p_n \langle n | A_I | n \rangle = \langle A \rangle$$

Comparing this with the expression for the linear response function, we find

$$R^{(1)}(\tau) = -\frac{i}{\hbar} \langle [A_I(\tau), A_I(0)] \rangle \quad \tau \geq 0$$

$$= 0 \quad \tau < 0$$

or as it is sometimes written with the unit step function:

$$\Rightarrow R^{(1)}(\tau) = -\frac{i}{\hbar} \Theta(\tau) \langle [A_I(\tau), A_I(0)] \rangle$$

Note that the time development of the system with the applied external field is governed by the dynamics of the equilibrium system. All of the time-dependence in the response function is under H_0 .

The response function is proportional to the difference of two complex correlation functions:

$$R^{(1)}(\tau) = -\frac{i}{\hbar} \{ \langle A_I(\tau) A_I(0) \rangle - \langle A_I(0) A_I(\tau) \rangle \}$$

$$= -\frac{i}{\hbar} (C_{AA}(\tau) - C_{AA}^*(\tau))$$

$$= \frac{2}{\hbar} C''(\tau) \quad \text{where } C''(\tau) = \text{Im}[C(\tau)]$$

If we express the correlation function in the eigenstate description:

$$C(\tau) = \sum_{n,j} p_n |A_{jn}|^2 e^{-i\omega_{jn}\tau}$$

then

$$R^{(1)}(\tau) = \frac{2}{\hbar} \sum_{n,j} p_n |A_{jn}|^2 \sin \omega_{jn}\tau$$

Note that $R^{(1)}(\tau)$ is real!

Alternatively, in the density matrix representation,

$$\begin{aligned}
 R^{(1)}(\tau) &= -\frac{i}{\hbar} (C_{AA}(\tau) - C_{AA}^*(\tau)) \\
 &= -\frac{i}{\hbar} \left\{ \text{Tr}(A_I(\tau)A_I(0)\rho_{eq}) - \text{Tr}(A_I(0)A_I(\tau)\rho_{eq}) \right\} \\
 &= -\frac{i}{\hbar} \text{Tr}([A_I(\tau), A_I(0)]\rho_{eq})
 \end{aligned}$$

The response function and energy absorption

Let's investigate the relationship between the linear response function and the absorption of energy from an external field

$$H = H_0 - f(t)A = H_0 - \mu \cdot E(t)$$

This expression gives the energy of the system, so the rate of energy absorption averaged over the non-equilibrium ensemble is described by:*

$$\frac{\partial \bar{H}}{\partial t} = -\frac{\partial f}{\partial t} \overline{A(t)}.$$

The time-averaged rate of energy absorption:

$$\begin{aligned}
 \dot{q} &= \frac{1}{T} \int_0^T dt \left[-\frac{\partial f}{\partial t} \overline{A(t)} \right] \\
 &= \frac{1}{T} \int_0^T dt \frac{\partial f(t)}{\partial t} \left[\langle A \rangle + \int_0^\infty d\tau R^{(1)}(\tau) f(t-\tau) \right]
 \end{aligned} \tag{1}$$

where

$$R^{(1)}(\tau) = -\frac{i}{\hbar} \langle [A_I(\tau), A_I(0)] \rangle$$

* See Wang (1985).

If we have a monochromatic light source:

$$f(t) = E_0 \cos \omega t = \frac{1}{2} [E_0 e^{-i\omega t} + E_0^* e^{i\omega t}] \quad (2)$$

Looking at the second term in (1):

$$\begin{aligned} & \frac{1}{2} \int_0^\infty d\tau R^{(1)}(\tau) [E_0 e^{-i\omega(t-\tau)} + E_0^* e^{i\omega(t-\tau)}] \\ & = \frac{1}{2} [E_0 e^{-i\omega t} \chi(\omega) + E_0^* e^{i\omega t} \chi(-\omega)] \end{aligned} \quad (3)$$

Differentiating (2) and plugging into (1) we have:

$$\dot{q} = -\frac{1}{T} \langle A \rangle [f(T) - f(0)] - \frac{1}{T} \int_0^T dt \frac{1}{2} [-i\omega E_0 e^{-i\omega t} + i\omega E_0^* e^{i\omega t}] \times \frac{1}{2} [E_0 e^{-i\omega t} \chi(\omega) + E_0^* e^{i\omega t} \chi(-\omega)]$$

Let's cycle average this expression (set $T = 2\pi / \omega$). First term vanishes. Cross terms in second integral vanish.

$$\begin{cases} \frac{1}{T} \int_0^T dt e^{-i\omega t} e^{+i\omega t} = 1 \\ \frac{1}{T} \int_0^T dt e^{-i\omega t} e^{-i\omega t} = 0 \end{cases}$$

$$\therefore \dot{q} = \frac{i}{4} \omega |E_0|^2 [\chi(-\omega) - \chi(\omega)]$$

$$\dot{q} = \frac{\omega}{2} |E_0|^2 \chi''(\omega)$$

The absorption of energy by the system is related to the imaginary part of the susceptibility!

$$\alpha(\omega) = \frac{\dot{q}}{\dot{E}_{in}} = \frac{4\pi\omega}{c} \chi''(\omega) \quad \dot{E}_{in} = \frac{c}{8\pi} |E_0|^2$$

- The absorption lineshape is related to the imaginary part of χ and
- χ is related to the Fourier transform of the correlation function that describes the fluctuations and dynamics of the equilibrium system $[C_{AA}(t)]$.

$$\begin{aligned}\chi''(\omega) &= \frac{1}{2i}(\chi(\omega) - \chi(-\omega)) \\ &= \frac{1}{2\hbar} \left\{ \int_0^\infty dt e^{i\omega t} [C_{AA}(t) - C_{AA}(-t)] - \int_0^\infty dt e^{-i\omega t} [C_{AA}(t) - C_{AA}(-t)] \right\} \\ &= \frac{1}{2\hbar} (C_{AA}(\omega) - C_{AA}(-\omega))\end{aligned}$$

\nwarrow
 $\int_0^\infty dt' e^{i\omega t'} [C_{AA}(-t') - C_{AA}(t')]$
 $= \int_{-\infty}^0 dt' e^{i\omega t'} [C_{AA}(t') - C_{AA}(-t')]$

From problem set: the correlation function obeys the detailed balance condition:

$$C_{AA}(-\omega) = e^{-\beta\hbar\omega} C_{AA}(\omega)$$

This relationship reflects the fact that upward and downward transition rates between states separated by ω are related by the population difference. Remember, from F.G.R. that the rates k are directly proportional to C_{AA} .

This allows us to write:

$$C_{AA}(\omega) \pm C_{AA}(-\omega) = (1 \pm e^{-\beta\hbar\omega}) C_{AA}(\omega)$$

So

$$\begin{aligned}\chi''(\omega) &= \frac{1}{2\hbar} (1 - e^{-\beta\hbar\omega}) C_{AA}(\omega) \\ &= \frac{1}{2\hbar} (1 - e^{-\beta\hbar\omega}) \int_{-\infty}^{+\infty} e^{i\omega t} \langle A(t) A(0) \rangle dt\end{aligned}$$

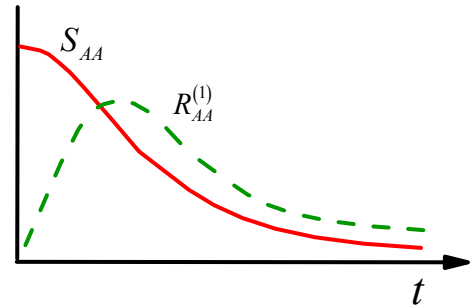
This is the result from before – the absorption of energy is dictated by the equilibrium fluctuations of the system. Inserting into $\alpha(\omega)$ in the previous page we have the result from

earlier:
$$\alpha(\omega) = \frac{2\pi\omega}{\hbar c} (1 - e^{-\beta\hbar\omega}) \int_{-\infty}^{+\infty} e^{i\omega t} \langle A(t) A(0) \rangle dt$$

Relaxation of a prepared state

The impulse response function $R^{(1)}(t)$ describes the behavior of a system initially at equilibrium that is driven by an external field. To describe the relaxation of a prepared state, the system must initially be in a non-equilibrium state, and then we will

watch the return to equilibrium. This behavior is described by step response function S_{AA} , which describes the behavior when a system held away from equilibrium by an external field is suddenly released. Just as we expect that the impulse response to rise from zero and be expressed as an odd function in time, the step response should decay from a fixed value and look even in time.



The step response comes from holding the system with a constant field $H = H_0 - fA$ until a time t_0 when the system is released, and it relaxes to the state $H = H_0$. You expect to describe this behavior by integrating the impulse response over all times $< t_0$.

- Response Functions are real.
- Quantum Correlation Functions are complex: $C(-t) = C^*(t)$
- Classical Correlation Functions are real and even: $C(t) = C(-t)$

For relaxation in terms of a real observable that is even in time, we construct a symmetrized function:

$$\begin{aligned} S_{AA}(t) &= \frac{1}{2} \left\{ \langle A_I(t) A_I(0) \rangle + \langle A_I(0) A_I(t) \rangle \right\} = \frac{1}{2} \left[\langle A_I(t), A_I(0) \rangle \right]_+ \\ &= \frac{1}{2} \{ C_{AA}(t) + C_{AA}(-t) \} \\ &= C'_{AA}(t) \end{aligned}$$

S is related to the real part of the correlation function, and defined for $t \geq 0$. The impulse response is related to the time-derivative of the step response, and in the classical limit

$$R^{(1)}(t) = \frac{1}{kT} \frac{d}{dt} S_{AA}(t) \quad (\text{high } T \text{ limit})$$

If we define $S_{AA}(\omega) = \frac{1}{2\pi} \int_0^\infty dt S_{AA}(t) e^{i\omega t}$, then

$$S_{AA}(\omega) = \frac{1}{2} [C_{AA}(\omega) + C_{AA}(-\omega)] = \frac{1}{2} (1 + e^{-\beta\hbar\omega}) C_{AA}(\omega)$$

$$\chi''(\omega) = \frac{1}{\hbar} \tanh\left(\frac{\beta\hbar\omega}{2}\right) S_{AA}(\omega) \quad \Rightarrow \quad \frac{\omega}{2kT} S_{AA}(\omega) \quad (\text{classical limit})$$

This is the fluctuation-dissipation theorem (Chemistry Nobel Prize, 1968; proven in 1951 by Callen and Welton).

Lars Onsager (1930): The relaxation of macroscopic non-equilibrium disturbance is governed by the same laws as the regression of spontaneous microscopic fluctuations in an equilibrium state.