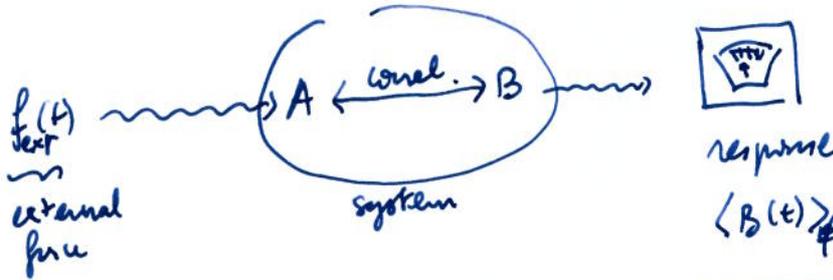


Chapter 2. Quantum linear response theory

Remind the initial motivation:



$$\langle B(t) \rangle_{f_{\text{ext}}} = \langle B \rangle_{\text{eq}} + \int dt' \chi_{BA}(t-t') f_{\text{ext}}(t') + \dots$$

Q: Given A , B and $H_{\text{pert}}(t) = -f(t) \cdot A$ what is χ_{BA} ?
 ex: Atom $B=A \rightarrow$ dipole $f \rightarrow$ e-m. field

The Fokker-Planck approach has furnished an answer (for $\hbar=0$) assuming a Markovian dynamics.

Can we ~~also~~ formulate the problem in a quantum frame?

I. Notations, basic tools (correlation functions)

A. Notation.

\hat{H}_0 : Hamiltonian of the system

$\{E_n, |\psi_n\rangle\}$: its spectrum (stationary states)

\hat{A}, \hat{B} : two observables.

B. Density matrix

Deterministic evolution $|\psi(t)\rangle$ obeys $i\hbar \frac{d}{dt} |\psi(t)\rangle = \hat{H}_0 |\psi(t)\rangle$

Q: what about the case with uncertainty on the state?
 \Rightarrow concept of density matrix $\hat{\rho}$

• Pure state $\hat{\rho} = |\psi_a\rangle \langle \psi_a|$

$$\langle A \rangle_{|\psi\rangle} = \langle \psi | \hat{A} | \psi \rangle = \text{Tr} \{ \hat{\rho} \hat{A} \}$$

• Statistical mixture: $\hat{\rho} = \sum_a P_a |\psi_a\rangle \langle \psi_a|$
 probab. to occupy state $|\psi_a\rangle$

$$\langle A \rangle = \sum_a P_a \langle \psi_a | \hat{A} | \psi_a \rangle = \text{Tr} \{ \hat{\rho} \hat{A} \}$$

quantum averaging
stat. averaging

Property: $\text{Tr}\{\rho\} = \sum_a P_a = 1$ (normalisation)

• Time evolution: von Neumann eq. (quantum Liouville eq.)

$\rho(t)$ evolves like $|\psi(t)\rangle\langle\psi(t)|$

\Downarrow

$$\frac{d}{dt} \hat{\rho}(t) = \frac{i}{\hbar} [\hat{\rho}(t), \hat{H}]$$

⚠ $\rho(t)$ is not an observable.

$$\frac{d}{dt} \langle \hat{A} \rangle_{\psi(t)} = \frac{i}{\hbar} \langle [\hat{H}, \hat{A}] \rangle_{\psi(t)}$$

• Schrödinger vs Heisenberg picture.

$\rho(t) \leftrightarrow |\psi(t)\rangle$

A : no time dependence

$\Rightarrow \langle A(t) \rangle = \text{Tr}\{\hat{\rho}(t) \hat{A}\}$
Schrödinger repres.

Heisenberg picture: $\hat{A}_H(t) = e^{\frac{i\hat{H}t}{\hbar}} \hat{A} e^{-\frac{i\hat{H}t}{\hbar}}$ (if H is indep. on t)

$|\psi(0)\rangle$: no time dependence
 $\rho(0)$

$$\frac{d}{dt} \hat{A}_H(t) = \frac{i}{\hbar} [\hat{H}, \hat{A}_H(t)]$$

$$\langle A(t) \rangle = \text{Tr}\{\rho(0) \hat{A}_H(t)\}$$

the same

~~C. Correlation functions. \rightarrow play a major role in ER~~

~~consider pairs of operators (A, B)~~

~~parametrized.~~

~~$\langle \rho_{BA}(t) \rangle$ and $\langle \rho_{AB}(t) \rangle$~~

• Equilibrium

Thermal equilibrium \rightarrow

Canonical (one body)

$$\rho_0 = \frac{1}{Z_0} e^{-\beta H_0}$$

\rightarrow grand canonical (many body)

$$e^{-\beta(H_0 - \mu N)}$$

C. Correlation functions

→ play a central role in linear response theory
 (lecture on FPE → χ_{BA} is a correlation fun)

consider a pair of operators \hat{A} and \hat{B}
 $\langle \hat{B}(t) \hat{A} \rangle$, $\langle [\hat{B}(t), \hat{A}] \rangle$, etc.

1. Unsymmetrized.

$$C_{BA}(t) = \langle \hat{B}(t) \hat{A} \rangle$$

↑ ↑
non commutating.

spectral representation: $\langle \dots \rangle = \text{Tr} \{ \rho \dots \} = \sum_n P_n \langle \Psi_n | \dots | \Psi_n \rangle$

$$C_{BA}(t) = \sum_{n,m} P_n B_{nm} A_{mn} e^{i\omega_{nm}t}$$

↓
Canonical $P_n \propto e^{-\beta E_n}$

$\omega_{nm} = \frac{E_n - E_m}{\hbar}$

↓
Fourier $\int dt e^{i\omega t} \dots$

$$\tilde{C}_{BA}(\omega) = 2\pi \sum_{n,m} P_n B_{nm} A_{mn} \delta(\omega + \omega_{nm})$$

2. Detailed balance.

$$C_{BA}(-t) = \langle B(-t) A \rangle = \langle B A(t) \rangle$$

↑ eq. ⇒ transp. inv.

classically: ($\hbar=0$) $= \langle A(t) B \rangle = C_{AB}(t)$

in particular $C_{AA}(-t) = C_{AA}(t)$

$$\tilde{C}_{AA}(-\omega) = \tilde{C}_{AA}(\omega) \quad (\hbar=0)$$

$\hbar \neq 0$:

$$\begin{aligned} \tilde{C}_{BA}(-\omega) &= 2\pi \sum_{n,m} P_n B_{nm} A_{mn} \delta(\omega - \omega_{nm}) \\ &= 2\pi \sum_{m,n} P_m A_{mn} B_{nm} \delta(\omega + \omega_{nm}) \end{aligned}$$

↓
 $P_m \propto e^{-\beta E_m} \Rightarrow P_m = P_n e^{\hbar\beta\omega_{nm}}$

$$\tilde{C}_{BA}(-\omega) = \tilde{C}_{AB}(\omega) e^{-\beta\hbar\omega}$$

Quantum asymmetry between $\omega \leftrightarrow -\omega$. ($\tilde{C}_{AA}(-\omega) = \tilde{C}_{AA}(\omega) e^{-\beta\hbar\omega}$)
 For $\omega > 0$ $\tilde{C}_{AA}(-\omega) < \tilde{C}_{AA}(\omega)$ | this is the asymmetry between absorption/emission
 cf. Exercise. II-3

3. Symmetrized correl. fun.

$$S_{BA}(t) = \frac{1}{2} \langle \{ \hat{B}(t), \hat{A} \} \rangle = \frac{1}{2} [C_{BA}(t) + C_{AB}(-t)]$$

4. Spectral function

$$\xi_{BA}(t) \stackrel{\text{def}}{=} \frac{1}{2\hbar} \langle [\hat{B}(t), \hat{A}] \rangle$$

→ ensures that $\lim_{\hbar \rightarrow 0} \xi_{BA}(t) \neq 0$

Spectral repres:
$$\tilde{\xi}_{BA}(\omega) = \frac{\pi}{\hbar} \sum_{n,m} (P_n - P_m) B_{nm} A_{mn} \delta(\omega + \omega_{nm})$$

Q: what is the classical limit of $\xi_{BA}(t)$?

Preliminary: $A(t) = e^{iH_0 t / \hbar} A e^{-iH_0 t / \hbar}$ (Heisenberg)

operator "velocity" $\dot{A} = \frac{i}{\hbar} [H_0, A]$

$\underline{x}: \vec{r} \rightarrow \dot{\vec{r}} = \vec{v} = \frac{\vec{p}}{m}$
operator (no t depend.)

we can write $A(t) - A(0) = \int_0^t dt' \dot{A}(t')$
Heisenberg repres. ↓ Heisenberg repres. of \dot{A}

$t = -i\hbar\beta$
 $\times \rho_0 = \frac{e^{-\beta H_0}}{Z_0} \left(e^{\beta H_0} A e^{-\beta H_0} - A = -i\hbar \int_0^\beta d\lambda \dot{A}(-i\hbar\lambda) \right)$
 $[A, \rho_0] = -i\hbar \rho_0 \int_0^\beta d\lambda \dot{A}(-i\hbar\lambda) \quad (*)$

Consider 2: $\xi_{BA}(t) = \frac{i}{\hbar} \langle [B(t), A] \rangle = \frac{i}{\hbar} \text{Tr} \{ \rho_0 [B(t), A] \}$
 $\text{Tr} \{ [A, \rho_0] B(t) \}$
use (*)

2: $\xi_{BA}(t) = \int_0^\beta d\lambda \text{Tr} \{ \rho_0 \dot{A}(-i\hbar\lambda) B(t) \} = \int_0^\beta d\lambda \langle \dot{A}(-i\hbar\lambda) B(t) \rangle$
now convenient for $\hbar \rightarrow 0$

5. Kubo correlation function

$$K_{BA}(t) \stackrel{\text{def}}{=} \int_0^\beta \frac{d\lambda}{\beta} \langle \underbrace{A(-i\hbar\lambda)}_{e^{\lambda H_0} A e^{-\lambda H_0}} B(t) \rangle$$

careful: no dot

physical meaning \rightarrow latter...

Relation to $\tilde{\Sigma}_{BA}(t)$

$$\tilde{\Sigma}_{BA}(t) = \frac{1}{2i} \int_0^\beta d\lambda \langle \underbrace{\dot{A}(-i\hbar\lambda)}_{\langle \dot{A}(-i\hbar\lambda-t) B \rangle} B(t) \rangle = \frac{\beta}{2i} K_{BA}^{\circ}(t) = -\frac{\beta}{2i} \frac{d}{dt} K_{BA}(t)$$

$$\boxed{\tilde{\Sigma}_{BA}(t) = i \frac{\beta}{2} \frac{d}{dt} K_{BA}(t)} \quad (**)$$

classical limit

$$\langle \underbrace{\hat{B}(t) \hat{A}}_{\text{quantum operator}} \rangle \xrightarrow{\hbar \rightarrow 0} \langle \underbrace{B(t) A}_{\text{classical observables}} \rangle = C_{BA}^{\text{class}}(t)$$

$$\text{obviously: } K_{BA}(t) \xrightarrow{\hbar \rightarrow 0} C_{BA}^{\text{class}}(t)$$

$$\tilde{\Sigma}_{BA}(t) \xrightarrow{\hbar \rightarrow 0} i \frac{\beta}{2} \frac{d}{dt} C_{BA}^{\text{class}}(t)$$

$$\ll \frac{1}{\hbar} [\dots, \dots] \xrightarrow{\hbar \rightarrow 0} i \beta \frac{d}{dt} \gg$$

Spectral representation

$$\tilde{K}_{BA}(\omega) = \int_0^\beta \frac{d\lambda}{\beta} \sum_{n,m} P_n A_{nm} e^{\lambda(\epsilon_n - \epsilon_m)} B_{mn} 2\pi \delta(\omega + \omega_{mn})$$

$$= \sum_{n,m} P_n \underbrace{\frac{e^{\beta\hbar\omega_{nm}} - 1}{\beta\hbar\omega_{nm}}}_{\frac{P_m - P_n}{\beta\hbar\omega_{nm}}} A_{nm} B_{mn} 2\pi \delta(\omega + \omega_{mn})$$

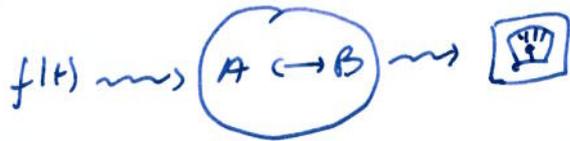
$n \leftrightarrow m$
 \rightarrow recover $\tilde{\Sigma}_{BA}(\omega)$

$$\boxed{\tilde{K}_{BA}(\omega) = \frac{\tilde{\Sigma}_{BA}(\omega)}{\beta\hbar\omega}}$$

which is the same as (**)

II. Linear response theory

A. Perturbation



$$\hat{H}_{\text{pert}}(t) = -f(t) \hat{A}$$

$$\hat{H}(t) = H_0 + \hat{H}_{\text{pert}}(t)$$

ex: Atom:

$$-\vec{A}(t) \cdot \frac{q\vec{P}}{m}$$

$$\hat{B} \rightarrow \hat{d} = q \cdot \vec{r}$$

B. Time evolution

$$\frac{d}{dt} \rho(t) = \frac{i}{\hbar} [\rho(t), H(t)]$$

Interaction representation

: extract the free evolution

$$\tilde{\rho}(t) \stackrel{\text{def}}{=} e^{iH_0 t/\hbar} \rho(t) e^{-iH_0 t/\hbar}$$

Inter. Schwöd.

$$B(t) \stackrel{\text{def}}{=} e^{iH_0 t/\hbar} B e^{-iH_0 t/\hbar}$$

interaction repres.

$$\langle B(t) \rangle_t = \text{Tr} \left\{ \underbrace{\rho(t)}_{\text{all time evolution}} B \right\} = \text{Tr} \left\{ \underbrace{\tilde{\rho}(t)}_{\substack{\text{time evol.} \\ \text{due to} \\ H_{\text{pert.}}}} \underbrace{B(t)}_{\substack{\text{time evol.} \\ H_0}} \right\}$$

$$\frac{d}{dt} \tilde{\rho}(t) = \frac{i}{\hbar} [\cancel{H_0}, \tilde{\rho}] + \frac{i}{\hbar} e^{iH_0 t} \underbrace{[\rho, H]}_{[\rho, H_0] + [\rho, H_{\text{pert}}]} e^{-iH_0 t}$$

$$= \frac{i}{\hbar} e^{iH_0 t} [\rho, H_{\text{pert}}] e^{-iH_0 t}$$

$$\hat{H}_I(t) \stackrel{\text{def}}{=} e^{iH_0 t} \hat{H}_{\text{pert}}(t) e^{-iH_0 t} = -f(t) \hat{A}(t)$$

$$\Rightarrow \boxed{\frac{d}{dt} \tilde{\rho}(t) = \frac{i}{\hbar} [\tilde{\rho}(t), \hat{H}_I(t)]}$$

C. Perturbation theory and response fct

$$\tilde{\rho} = \tilde{\rho}^{(0)} + \tilde{\rho}^{(1)} + \tilde{\rho}^{(2)} + \dots \quad : \text{ powers in } f$$

$$\tilde{\rho}^{(n)} = \mathcal{O}(f^n)$$

$$\tilde{\rho}^{(0)} = \rho_0 = \frac{e^{-\beta H_0}}{Z_0}$$

recurrence:

$$\frac{d}{dt} \tilde{\rho}^{(n)} = \frac{i}{\hbar} [\tilde{\rho}^{(n-1)}(t), H_I(t)]$$

Assume $f(t) \rightarrow 0$ as $t \rightarrow -\infty$ (start from equilibrium at $-\infty$)

$$\tilde{\rho}^{(n)}(t) = -\frac{i}{\hbar} \int_{-\infty}^t dt' f(t') [\tilde{\rho}^{(n-1)}(t'), A(t')]$$

at lowest order:

$$\tilde{\rho}(t) = \rho_0 - \frac{i}{\hbar} \int_{-\infty}^t dt' f(t') [\rho_0, A(t')] + \mathcal{O}(f^2)$$

This can be used to extract the linear response fct:

Def: $\langle B(t) \rangle_f \stackrel{\text{def}}{=} \langle B \rangle_{\rho_0} + \int dt' \chi_{BA}(t-t') f(t') + \mathcal{O}(f^2)$

$$\langle B(t) \rangle_f = \text{Tr} \{ \tilde{\rho}(t) B(t) \}$$

$$= \text{Tr} \{ \rho_0 B \} - \frac{i}{\hbar} \int_{-\infty}^t dt' f(t') \text{Tr} \{ [\rho_0, A(t')] B(t) \} + \dots$$

$$= \langle B(t) \rangle_{\rho_0} - \langle [B(t), A(t')] \rangle$$

$$\chi_{BA}(t) = \frac{i}{\hbar} \theta(t) \langle [B(t), A] \rangle = 2i \theta(t) \chi_{BA}^{\text{eq}}(t) = \theta(t) \beta K_{BA}(t)$$



Lehman (spectral) representation

$$\int_0^{\infty} dt e^{i\Omega t} = \frac{1}{0^+ - i\Omega} = \frac{i}{\Omega + i0^+}$$

\uparrow
 $e^{-0^+ t}$

very important.
 \leftrightarrow causality

$$\chi_{BA}(t) = \frac{i}{\hbar} \theta(t) \sum_{n,m} (P_n - P_m) B_{nm} A_{mn} e^{i\omega_{nm}t}$$

$$\tilde{\chi}_{BA}(\omega) = -\frac{1}{\hbar} \sum_{n,m} (P_n - P_m) B_{nm} A_{mn} \frac{1}{\omega + \omega_{nm} + i0^+}$$

Remark: using $\tilde{\chi}_{BA}(\omega) = \frac{\pi}{\hbar} \sum_{n,m} (P_n - P_m) B_{nm} A_{mn} \delta(\omega + \omega_{nm})$

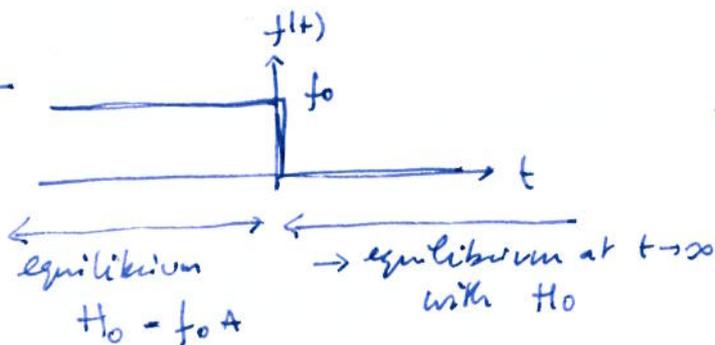
we deduce:

$$\tilde{\chi}_{BA}(\omega) = - \int \frac{d\omega'}{\pi} \frac{\tilde{\chi}_{BA}(\omega')}{\omega - \omega' + i0^+} = \int \frac{d\omega'}{\pi} \frac{\tilde{\chi}_{BA}(\omega')}{\omega' - \omega} + i \tilde{\chi}_{BA}(\omega)$$

if $B = A^+ \Rightarrow \tilde{\chi}_{A+A}(\omega)$ is real

$$\text{then } \text{Im } \tilde{\chi}_{A+A}(\omega) = \tilde{\chi}_{A+A}(\omega)$$

Relaxation



\Rightarrow relaxation experiment
 $\hat{=}$ standard in magnetism.
 (switch off the B-field)

$$f(t) = f_0 \theta(-t)$$

$$\underline{t > 0}: \langle B(t) \rangle_+ \equiv \langle B \rangle_{eq} + \int dt' \underbrace{\chi_{BA}(t-t')}_{\leftrightarrow K_{BA}(t)} \underbrace{f(t')}_{f_0 \theta(-t')} + O(f^2)$$

$$= \langle B \rangle_{eq} + f_0 \beta K_{BA}(t) + O(f^2)$$

this shed a new light on the relation

$$\underbrace{\chi_{BA}(t)}_{\text{response}} = -\theta(t) \beta \frac{d}{dt} \underbrace{K_{BA}(t)}_{\text{relaxation}}$$

D. Generalised fluctuation-dissipation theorem

Dissipation: $H_{\text{pert}}(t) = -f(t)A$

$$P_{\text{diss}} = \overline{f(t) \dot{A}(t)}_f$$

\downarrow
controlled by $X_{AA}(t)$

$$P_{\text{dissip}} = \frac{1}{2} \omega f \omega^2 \underbrace{\text{Im}[\tilde{X}_{AA}(\omega)]}_{\tilde{\chi}_{AA}(\omega)}$$

$$= \frac{1}{2} f \omega^2 \text{Re}[Y(\omega)]$$

where $Y(\omega) = \tilde{X}_{AA}(\omega)$
 $= -i\omega \tilde{\chi}_{AA}(\omega)$

Spectral series for \tilde{C}_{BA} and $\tilde{\chi}_{BA}$

$$\tilde{\chi}_{BA}(\omega) = \frac{\pi}{\hbar} \sum_{n,m} (P_n - P_m) B_{nm} A_{nm} \delta(\omega + \omega_{nm})$$

\downarrow
 $P_m = P_n e^{\beta \hbar \omega_{nm}}$

$\omega_{nm} \rightarrow -\omega$

$$= (1 - e^{-\beta \hbar \omega}) \frac{\pi}{\hbar} \sum_{n,m} P_n B_{nm} A_{nm} \delta(\omega)$$

$$\tilde{C}_{BA}(\omega) = \frac{2\hbar}{1 - e^{-\beta \hbar \omega}} \tilde{\chi}_{BA}(\omega)$$

for $B=A$

$$\underbrace{\tilde{C}_{AA}(\omega)}_{\text{fluct.}} = \frac{2\hbar}{1 - e^{-\beta \hbar \omega}} \underbrace{\tilde{\chi}_{AA}(\omega)}_{\text{dissip.}}$$

Eq: $\boxed{\hbar \rightarrow 0}$

$$\tilde{C}_{BA}(\omega) = \frac{2}{\beta \omega} \tilde{\chi}_{BA}(\omega)$$

$$\underbrace{\tilde{C}_{BA}(\omega)}_{\text{diss.}} \downarrow = -\beta \theta(t) \frac{d}{dt} C_{BA}^{\text{diss}}(t)$$

Application: Quantum generalisation of Johnson-Nyquist th.



$\delta I = \delta I = 0$

Johnson & Nyquist (1928)
 $\langle |V_{\omega}|^2 \rangle = 2 k_B T \times R$

power spectrum $\tilde{S}_{VV}(\omega) = \int dt e^{i\omega t} \langle V(t)V \rangle$

Nyquist (1928) $k_B T = \text{energy of harm. osc.}$
 $\hookrightarrow k_B T \rightarrow \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} ?$

Model: $\hat{H}_{\text{ext}}(t) = V_{\text{ext}}(t) \hat{Q}$
 \hat{Q} natural observable

Admittance = Conductance $G(\omega) = \tilde{\chi}_{II}(\omega)$
 i.e. $\langle I \omega \rangle = G(\omega) V_{\omega}$

Current fluctuations. FDT: $\tilde{C}_{II}(\omega) = \frac{2\hbar}{1 - e^{-\beta \hbar \omega}} \tilde{\chi}_{II}(\omega)$
 $\tilde{C}_{II}(\omega) = \frac{2\hbar \omega}{1 - e^{-\beta \hbar \omega}} \text{Re}[G(\omega)]$
 $2\hbar \omega \left(\frac{1}{e^{\beta \hbar \omega} - 1} + i \right)$ absorption emission ($\omega > 0$)
 $\text{Im}[\tilde{\chi}_{II}(\omega)] + i\omega \tilde{\chi}_{II}(\omega)$

Symmetrised correlator: $\tilde{S}_{II}(\omega) = \frac{\tilde{C}_{II}(\omega) + \tilde{C}_{II}(-\omega)}{2}$
 $= 2 \left(\frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} + \frac{\hbar \omega}{2} \right) \text{Re}[G(\omega)]$

Voltage fluctuations $\times \frac{1}{|G(\omega)|^2}$ $\nearrow \frac{2k_B T R}{\hbar \omega}$

$\langle |V_{\omega}|^2 \rangle \equiv \tilde{S}_{VV}(\omega) = \text{Re}[z(\omega)] \times \hbar \omega \coth \frac{\hbar \omega}{2k_B T}$
 $= 2 \times \left(\frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} + \frac{\hbar \omega}{2} \right) \text{Re}[z(\omega)]$

Callen & Welton, 1951

measurement: Koch (1981)

interpretation: both emission and absorption contribute to the potential fluctuations.