III. Response Functions (Altland & Simons, Chapter 7)

III.1 Experimental techniques

Three broad categories of experimental condensed matter physics:

- thermodynamics
- transport
- spectroscopy

Thermodynamic information can be computed theoretically by differentiating the partition function Z with respect to a few global variables (temperature, magnetic field, pressure, ...)

$\longrightarrow$ highly universal $\oplus$

$\longrightarrow$ no information on spatial structures, dynamical features $\ominus$

$\Longrightarrow$ thermodynamics do not suffice to fully understand the physics of a system, in particular its <u>microscopic structure</u>

Transport & spectroscopy experiments, generic features:

- use electromagnetic forces as perturbation
  - photons (Optics, X-ray scattering)
  - voltage drop (transport)
  - spin magnetic moments (e.g., neutron scattering)
- response of the system probed by a detector

Formalism: Linear-response theory

skipped

Time-dependent perturbation Hamiltonian

$$\hat{H}_F = \int d^d r \underbrace{F_i'(\vec{r},t)}_{\text{forces}} \underbrace{\hat{X}_i'(\vec{r})}_{\text{coupling operator}}$$

e.g.
$$F_i'(\vec{r},t) = \phi(\vec{r},t) = \text{electric voltage}$$
$$\hat{X}_i'(\vec{r}) = \hat{\rho}(\vec{r}) = \text{charge density}$$

- forces are assumed to be much weaker than the internal energy scales of the system
  → "perturbation"
- forces perturb system away from its reference state at $F_i' = 0$
  — this is not necessarily the equilibrium state! —

Thus some observables that are initially zero will change their value in response to the forces.

<u>Example:</u> voltage ϕ $\rightarrow$ current flow $\langle j \rangle \neq 0$

- The response of observable $X_i[F_j']$ is approximately linear provided that F_j' are sufficiently small:

$$\underbrace{X_i(\vec{r},t)}_{\substack{\text{externally}\\ \text{adjustable}}} = \int d^d r \int dt' \underbrace{\chi_{ij}(\vec{r},t;\vec{r}',t')}_{\text{kernel } \chi:\ \boxed{\text{intrinsic property of the system}}} \underbrace{F_j'(\vec{r}',t')}_{\substack{\text{externally}\\ \text{adjustable}}} + \mathcal{O}(F'^2)$$

χ = "response function", "generalized susceptibility"

<u>Experimental methods:</u>

- thermodynamics:
  - specific heat
  - magnetic susceptibility
  - compressibility
- transport:
  - electrical conductance $g = \frac{I}{U}$
  - thermal conductivity
  - spin currents
  - thermoelectric effects (Peltier, Seebeck.)

- spectroscopy:
  - Raman scattering
  - infrared spectroscopy
  - X-ray crystallography
  - X-ray /electron spectroscopy
  - X-ray fluorescence spectroscopy
  - photoemission spectroscopy
  - Auger spectroscopy
  - Neutron scattering
  - magnetic resonance
  - nuclear magnetic resonance (NMR), Knight shift (↔ Pauli paramagnetism), electron spin resonance (ESR)
  - ... many more

- important other technique: scanning tunneling microscopy (STM) and spectroscopy (STS)

skipped

III.2 Linear response theory (canonical formalism)

Experiment: switch on a small field $\delta h(\vec{r},t)$

Linear response: small deviations from thermal equilibrium

Assumption: Coupling of δh to observable $A(\vec{r})$:

$$\boxed{\begin{aligned} H(t) &= H_0 + H_1(t) \\ H_1(t) &= -\int d^3\vec{r}\; \delta h(\vec{r},t)\, A(\vec{r}) \end{aligned}}$$

Examples:
- $A(\vec{r}) \rightarrow \overleftrightarrow{\sigma}(\vec{r})$, $\delta h \rightarrow \mu_B \delta\vec{H}$
  (spin matrices) (magnetic field)
  $\Rightarrow$ magnetic susceptibility $\chi(\vec{q},\omega)$
- $A(\vec{r}) \rightarrow \vec{j}(\vec{r})$, $\delta h \rightarrow \frac{e}{c}\delta\vec{A}$
  (vector potential)
  $\Rightarrow$ optical conductivity $\overleftrightarrow{\sigma}(\omega)$

Strategy: Linear response from time-dependent perturbation theory

Question: how does $\langle B(\vec{r},t)\rangle$ change due to δh?

$$\boxed{\langle B(\vec{r},t)\rangle = \langle B(\vec{r})\rangle_{eq} + \delta\langle B(\vec{r},t)\rangle}$$

For $t \rightarrow -\infty$ the system is in thermal equilibrium

Schrödinger picture: $\langle B(\vec{r},t)\rangle = \mathrm{Tr}\left[\underbrace{\rho(t)}_{\text{density matrix}} B(\vec{r})\right]$; $\mathrm{Tr}[\rho(t)] = 1$

① Density matrix solves the von Neumann equation (keeping $\hbar$ alive here)

$$\boxed{i\hbar\,\partial_t\,\rho(t) = [H(t), \rho(t)]} \quad (*)$$

with initial condition $\rho(t\to-\infty) = \rho_0$

$$[H_0, \rho_0] = 0$$

Canonical ensemble: $\rho_0 = \dfrac{e^{-\beta H_0}}{\mathrm{Tr}[e^{-\beta H_0}]}$

Linear response: $\rho(t) = \rho_0 + \delta\rho(t)$

with $\boxed{i\hbar\,\partial_t\,\rho(t) = [H_0, \delta\rho(t)] + [H_1(t), \rho_0]} + \mathcal{O}(\delta h^2)$ (from $(*)$)

Solution: (**) $\boxed{\delta\rho(t) = \frac{1}{i\hbar}\int_{-\infty}^{t} d\tau\, e^{-iH_0(t-\tau)/\hbar}\,[H_1, \rho_0]\, e^{iH_0(t-\tau)/\hbar}}$

check: $\partial_t\,\delta\rho(t) = \frac{1}{i\hbar}\, e^{-iH_0(t-t)/\hbar}[H_1(t), \rho_0]\, e^{iH_0(t-t)/\hbar} -$

$$-\frac{i}{\hbar} H_0\,\delta\rho(t) + \frac{i}{\hbar}\,\delta\rho(t)\, H_0 \quad ✓$$

② Expectation value of observable B

$$\langle B(\vec r, t)\rangle = \mathrm{Tr}[\rho_0\, B(\vec r)] + \mathrm{Tr}[\delta\rho(t)\, B(\vec r)]$$

$$\delta\langle B(\vec r, t)\rangle = \mathrm{Tr}[\delta\rho(t)\, B(\vec r)] \overset{(**)}{=}$$

from $H_1 = \Theta\int A\,\delta h$

$$= (-)\frac{1}{i\hbar}\int_{-\infty}^{t} d\tau \int d^3 r'\, \mathrm{Tr}\Big[\big[\overbrace{e^{iH_0\tau/\hbar} A(\vec r')\, e^{-iH_0\tau/\hbar}}^{\equiv A(\vec r', \tau)\ \text{interaction picture}}, \rho_0\big] \times$$

$$\times \underbrace{\big[e^{iH_0 t/\hbar}\, B(\vec r)\, e^{-iH_0 t/\hbar}\big]}_{\equiv B(\vec r, t)} \times$$

$$+\ \delta h(\vec r, \tau)$$

$$= \ldots$$

use $\mathrm{Tr}\left[[a,b]c\right] = \mathrm{Tr}\left[[c,a]b\right]$

set $t' := T$

$$\ldots = \frac{i}{\hbar} \int_{-\infty}^{t} dt' \int d^3r' \underbrace{\mathrm{Tr}\left[\left[B(\vec r,t), A(\vec r\,',t')\right]\rho_0\right]}_{\langle [B,A] \rangle_{eq}} \delta h(\vec r\,',t')$$

<u>Result:</u>

$$\boxed{\delta \langle B(\vec r,t) \rangle = \frac{i}{\hbar} \int_{-\infty}^{t} dt' \int d^3r' \left\langle \left[B(\vec r,t), A(\vec r\,',t')\right] \right\rangle_{eq} \delta h(\vec r\,',t')}$$

<u>Remarks:</u>

(i) Convolution in real space & time

$\Longrightarrow$ product in Fourier space & frequency

(ii) the linear response function is thus defined as the retarded commutator

$$\boxed{\chi^R_{BA}(\vec r,t;\vec r\,',t') \equiv \frac{i}{\hbar} \left\langle \left[B(\vec r,t), A(\vec r\,',t')\right] \right\rangle_{eq} \Theta(t-t')}$$

(iii) if the equilibrium state is spatially and temporally translationally invariant:

$$\chi^R_{BA}(\vec r,t,\vec r\,',t') \equiv \chi^R_{BA}(\vec r-\vec r\,', t-t')$$

$\xRightarrow{\text{Fourier}}$ $\boxed{\delta \langle B(\vec q,\omega) \rangle = \chi^R_{BA}(\vec q,\omega)\, \delta h(\vec q,\omega)}$

convergence factor ensuring causality

with $\chi^R_{BA}(\vec q,\omega) \equiv \lim_{\eta\to 0^+} \int_{-\infty}^{\infty} dt \int d^3r\, e^{i\vec q\vec r} e^{i(\omega+i\eta)t} \chi^R_{BA}(\vec r,t)$

(iv) the retarded commutator is the Green's function

$$\chi^R_{BA}(\ldots) \equiv G^R_{BA}(\ldots)$$

[often used: G in real space, χ in Fourier space]

Mathematically G is the solution of a differential equation of motion, e.g. driven classical harmonic oscillator:

$$\left(\frac{d^2}{dt^2} + 2\lambda \frac{d}{dt} + \omega_0^2\right) x(t) = \frac{1}{m} f(t)$$

G fulfills

$$\left(\frac{d^2}{dt^2} + 2\lambda \frac{d}{dt} + \omega_0^2\right) G(t-t') = \delta(t-t')$$

Knowing G, x can be constructed:

$$x(t) = \int_{-\infty}^{\infty} dt'\, G(t-t')\, \frac{f(t')}{m}$$

which is exactly of the form

$$\text{"}\delta \langle B \rangle = \int \chi\, \delta h\text{"}$$

$$G \longleftrightarrow \chi$$

end lecture 5
1.5 hours

(a) Properties of the response function

Observables A and $\mathbb{B}$ are hermitean operators;
therefore (using G for the real space & time)

$\boxed{G^R_{BA} \text{ is real}}$

$$G^{R\,*}_{BA} = -\frac{i}{\hbar} \langle \underbrace{[B,A]^+}_{\substack{\shortparallel \\ [A^+,B^+] = -[B,A]}} \rangle_{eq} \, \Theta(t-t') = \ldots$$

$$\ldots = \frac{i}{\hbar} \langle [B,A] \rangle_{eq} \, \Theta(t-t') = G^R_{BA} \quad //$$

For $\chi_{BA}(\vec{q},\omega) = \chi'_{BA}(\vec{q},\omega) + i\,\chi''_{BA}(\vec{q},\omega)$

it follows that (suppressing $\vec{q}$)

$$\boxed{\begin{aligned} \chi'_{BA}(-\omega) &= \chi'_{BA}(\omega) && \text{real part even} \\ \chi''_{BA}(-\omega) &= -\chi''_{BA}(\omega) && \text{imag. part odd} \end{aligned}}$$

(b) Causality

The step function $\Theta(t-t')$ in $G^R_{BA}(t-t')$ is a consequence of causality: $B(t)$ can only be influenced by an earlier $\delta h(t')$, i.e. for $t \geq t'$. Later we will see how this influences analytical properties in the complex frequency plane.

(c) Lehmann representation

Assume that we know the exact eigenstates of H_0:

$$H_0 |n\rangle = E_n |n\rangle$$

The statistical operator for the canonical ensemble is

$$\frac{e^{-\beta H_0}}{Z} \longrightarrow \frac{e^{-\beta E_n}}{Z}, \quad Z = \mathrm{tr}\, e^{-\beta H_0} = \sum_n e^{-\beta E_n}$$

and

$$G^R_{AB}(t) = \frac{i}{\hbar}\Theta(t)\frac{1}{Z}\sum_{nn'} e^{-\beta E_n}\Big[\langle n|e^{iH_0t/\hbar} A e^{-iH_0t/\hbar}|n'\rangle\langle n'|B|n\rangle -$$

$$- \langle n|B|n'\rangle\langle n'|e^{iH_0t/\hbar} A e^{-iH_0t/\hbar}|n\rangle\Big]$$

$$= \frac{i}{\hbar}\Theta(t)\frac{1}{Z}\sum_{nn'} e^{-\beta E_n}\Big[e^{i(E_n-E_{n'})t/\hbar}\langle n|A|n'\rangle\langle n'|B|n\rangle$$

$$- e^{-i(E_n-E_{n'})t/\hbar}\langle n|B|n'\rangle\langle n'|A|n\rangle\Big]$$

Laplace transform

$$\int_0^\infty dt\, e^{i(\omega+i\eta)t}\, G^R_{AB}(t) \equiv \chi_{AB}(\omega+i\eta)$$

yields because of

$$\frac{i}{\hbar}\int_0^\infty dt\, e^{i(\omega+i\eta)t}\, e^{\pm i(E_n-E_{n'})t/\hbar} = -\frac{1}{\hbar(\omega+i\eta)\pm(E_n-E_{n'})}$$

the relation

$$\boxed{\chi_{AB}(\omega+i0) = -\frac{1}{Z}\sum_{nn'} e^{-\beta E_n}\left[\frac{\langle n|A|n'\rangle\langle n'|B|n\rangle}{\hbar\omega+E_n-E_{n'}+i0} - \frac{\langle n|B|n'\rangle\langle n'|A|n\rangle}{\hbar\omega-E_n+E_{n'}+i0}\right]}$$

In the thermodynamic limit the complex response function has a close sequence of poles slightly below the real axis at

$$\hbar\omega = \pm(E_n - E_{n'}) \underline{- i0}$$

The imaginary part is given via the Dirac relation

$$\frac{1}{\omega + i0} = \underbrace{\mathcal{P}\frac{1}{\omega}}_{\substack{\text{principal}\\ \text{value (under}\\ \text{integral)}}} - i\pi\,\delta(\omega)$$

by

$$\chi''_{AB}(\omega) = \pi \frac{1}{Z}\sum_{nn'} e^{-\beta E_n}\Big[\delta(\hbar\omega + E_n - E_{n'})\langle n|A|n'\rangle\langle n'|B|n\rangle$$

odd! ✓

$$- \underbrace{\delta(\hbar\omega - E_n + E_{n'})\langle n|B|n'\rangle\langle n'|A|n\rangle}_{\text{rename } n \leftrightarrow n'}\Big]$$

$$= \frac{\pi}{Z}\sum_{nn'} e^{-\beta E_n}\langle n|A|n'\rangle\langle n'|B|n\rangle\,\delta(\hbar\omega + E_n - E_{n'})$$

$$\times\left[1 - e^{-\beta\hbar\omega}\right].$$

Most important case: $A = B$

$$\boxed{\chi''_{AA}(\omega) = \pi\left(1 - e^{-\beta\hbar\omega}\right)\frac{1}{Z}\sum_{nn'} e^{-\beta E_n}|\langle n|A|n'\rangle|^2\,\delta(\hbar\omega + E_n - E_{n'})}$$

"Fermi's golden rule"

$$\boxed{\chi'_{AA}(\omega) = -\frac{1}{Z}\sum_{nn'}\mathcal{P}\frac{|\langle n|A|n'\rangle|^2}{\hbar\omega + E_n - E_{n'}}\left(e^{-\beta E_n} - e^{-\beta E_{n'}}\right)}$$

Some properties of response functions:

(i) selection rules: $\overbrace{\langle n|A|n'\rangle}^{\text{matrix elements}}$ imply that only certain states contribute to the response. For example: "dipole-allowed optical transitions" when A is proportional to the dipole operator, i.e. a laser can only excite from a state with even parity (s-orbital) to a state with odd parity (p-orbital) if the system is inversion-symmetric.

(ii) high-frequency limit $\lim_{\omega\to\infty} \chi_{AA}(\omega+i0) = \lim_{\omega\to\infty} \chi'_{AA}(\omega)$

$$\sim \frac{1}{\omega^2}$$

(iii) Energy dissipation: $\boxed{\omega \chi''_{AA}(\omega) \geq 0}$ — the system is "passive", i.e. the energy transferred to the system is ≥ 0

$$\left[\Delta E = \int \frac{d\omega}{2\pi} \int \frac{d^3q}{(2\pi)^3}\, \omega\, \chi''_{AA}(\vec{q},\omega)\, |\delta h(\vec{q},\omega)|^2 \geq 0\right]$$

(iv) Kramers-Kronig relations (useful in practice)

$$\chi'_{AA}(\omega) = -\frac{1}{\pi} \mathcal{P}\int_{-\infty}^{\infty} d\omega' \frac{\chi''_{AA}(\omega')}{\omega-\omega'}$$

$$\chi''_{AA}(\omega) = \frac{1}{\pi} \mathcal{P}\int_{-\infty}^{\infty} d\omega' \frac{\chi'_{AA}(\omega')}{\omega-\omega'}$$

III.3 Fluctuation-dissipation theorem

III.3.1 Correlation functions

So far we have looked at the response to a perturbation, which tells us about dissipation in a system: e.g., - optical absorption

- resistivity

Alternatively one can look at fluctuations, e.g., voltage fluctuations in an RC circuit or Brownian motion of particles in a liquid. To this end we define correlation functions

Correlation: $C_{AB}(\vec{r}t, \vec{r}'t') \equiv \langle A(\vec{r}t)\, B(\vec{r}'t')\rangle_{eq}$

fluctuation: $S_{AB}(\vec{r}t, \vec{r}'t') \equiv \Big\langle \big(A(\vec{r}t) - \langle A(\vec{r})\rangle_{eq}\big)\cdot\big(B(\vec{r}'t') - \langle B(\vec{r}')\rangle_{eq}\big)\Big\rangle_{eq}$

$$= C_{AB}(\vec{r}t, \vec{r}'t') - \langle A(\vec{r})\rangle_{eq} \langle B(\vec{r}')\rangle_{eq}$$

symmetrized: $\underbrace{\phi_{AB}(\vec{r}t, \vec{r}'t')}_{\in \mathbb{R}} \equiv \frac{1}{2}\left(C_{AB}(\vec{r}t, \vec{r}'t') + C_{BA}(\vec{r}'t', \vec{r}t)\right) - \langle A(\vec{r})\rangle_{eq}\langle B(\vec{r}')\rangle_{eq}$,

Since the equilibrium state is stationary we know that

$C_{AB}(t, t') = C_{AB}(t-t')$ etc.

We define Fourier transforms

$$S_{AB}(\omega) = \int_{-\infty}^{\infty} dt \; S_{AB}(t)\, e^{i\omega t} \quad \text{etc.}$$

For the observables we define

$$A(\omega) = \int_{-\infty}^{\infty} dt \; A(t)\, e^{i\omega t}$$

and therefore

$$\langle A(\omega)\, B(\omega')\rangle_{eq} = \int dt \int dt' \, e^{i\omega t + i\omega' t'} \, C_{AB}(t-t')$$

using $e^{i\omega t + i\omega' t'} = e^{i\omega(t-t') + i(\omega+\omega')t'}$

we obtain

$$\langle A(\omega)\, B(\omega')\rangle_{eq} = 2\pi\, \delta(\omega+\omega')\, C_{AB}(\omega)$$

$\Rightarrow$ correlations only between $A(\omega)$ and $B(-\omega)$, which follow from time-translational invariance $\Leftrightarrow$ energy conservation.

Also: $S_{AB}(\omega) = C_{AB}(\omega) - 2\pi\, \delta(\omega)\, \langle A\rangle_{eq} \langle B\rangle_{eq}$

end lecture 6
(1.5 hrs)

III.3.2 The fluctuation-dissipation theorem

Obviously there must be a relation between response functions like

$$\hat{\chi}''_{AB}(t-t') \equiv \frac{1}{2\hbar}\langle [A(t)B(t') - B(t')A(t)] \rangle$$

(commutator without Θ-fct.)

and correlation functions:

$$\hat{\chi}''_{AB}(t-t') = \frac{1}{2\hbar}\left[C_{AB}(t-t') - C_{BA}(t'-t)\right]$$

$$= \frac{1}{2\hbar}\left[S_{AB}(t-t') - S_{BA}(t'-t)\right].$$

Fourier transform:

$$\hat{\chi}''_{AB}(\omega) = \frac{1}{2\hbar}\left[S_{AB}(\omega) - S_{BA}(-\omega)\right] = \frac{1}{2\hbar}\left[C_{AB}(\omega) - C_{BA}(-\omega)\right].$$

In a canonical ensemble, which maximizes entropy, we have

$$\boxed{S_{BA}(-\omega) = e^{-\beta\hbar\omega} S_{AB}(\omega)}$$ detailed balance

$$\Rightarrow \boxed{\hat{\chi}''_{AB}(\omega) = \frac{1}{2\hbar}\left[1 - e^{-\beta\hbar\omega}\right] S_{AB}(\omega)}$$

fluctuation-dissipation theorem

mechanical quantity

statistical quantity

Proof:

$$C_{AB}(\vec{r},\vec{r}\,';t) = \frac{1}{Z}\mathrm{Tr}\left\{e^{-\beta H} e^{iHt} A(\vec{r}) e^{-iHt} B(\vec{r}\,')\right\}$$

$$C_{BA}(\vec{r}\,',\vec{r},-t) = \frac{1}{Z}\mathrm{Tr}\left\{e^{-\beta H} B(\vec{r}\,') e^{iHt} A(\vec{r}) e^{-iHt}\right\} =$$

$$= \frac{1}{Z}\mathrm{Tr}\left\{e^{iHt} A(\vec{r}) e^{-iHt} e^{-\beta H} B(\vec{r}\,')\right\} =$$

$$= \frac{1}{Z}\mathrm{Tr}\left\{e^{-\beta H} e^{iH(t-i\beta)} A(\vec{r}) e^{-iH(t-i\beta)} B(\vec{r}\,')\right\} =$$

$$= C_{AB}(\vec{r},\vec{r}\,';t-i\beta) \qquad [\hbar=1]$$

$$\Rightarrow C_{BA}(\vec{r}\,',\vec{r};-\omega) = \int dt\, e^{i\omega t} C_{AB}(\vec{r},\vec{r}\,';t-i\beta) \overset{t'=t-i\beta}{=}$$

$$= e^{-\beta\omega}\int dt'\, e^{i\omega t'} C_{AB}(\vec{r},\vec{r}\,';t') =$$

$$= e^{-\beta\omega}\, C_{AB}(\vec{r},\vec{r}\,';\omega) \quad //$$

$S_{AB}(\omega)$ differs from $C_{AB}(\omega)$ by $2\pi\delta(\omega)\langle A\rangle\langle B\rangle$, and since $e^{-\beta\omega}\delta(\omega) = \delta(\omega)$ one obtains

$$S_{BA}(\vec{r}\,',\vec{r};-\omega) = S_{AB}(\vec{r},\vec{r}\,';\omega)\, e^{-\beta\omega}. \quad //$$

Also one has $\hat{\chi}''_{AB}(\omega) = \frac{1}{2\hbar}\left(1-e^{-\beta\hbar\omega}\right) C_{AB}(\omega)$

$$\phi_{AB}(\omega) = \hbar\, \hat{\chi}''_{AB}(\omega) \coth\left(\frac{\hbar\omega}{2k_B T}\right)$$

[$\vec{r},\vec{r}\,'$ and $\vec{q}$ can be added]

Classical Limit:

$$\boxed{\hat{\chi}''_{AB}(\omega) \underset{\hbar\omega \ll k_B T}{=} \frac{\beta}{2}\omega\, S_{AB}(\omega)}$$

independent of $\hbar$

$\boxed{\text{Measuring response} \;\hat{=}\; \text{Measuring fluctuations in equilibrium}}$

Exercise:

Nyquist noise in a resistor

III.4 Linear response via functional derivatives

(see Altland & Simons, Chapter 7)

Response of an operator $\hat{X} = \sum_{aa'} c_a^+ X_{aa'} c_{a'}$

at imaginary times can be written as

$$X(\tau) = \sum_{aa'} \langle \bar{\psi}_a(\tau) X_{aa'} \psi_{a'}(\tau) \rangle$$

$$\langle \ldots \rangle \equiv \mathcal{Z}^{-1} \int \mathcal{D}(\bar{\psi},\psi)\, e^{-S[\underset{\substack{\uparrow \\ \text{force}}}{F'},\bar{\psi},\psi]}$$

with action $S[F',\bar{\psi},\psi] = \underbrace{S_0[\bar{\psi},\psi]}_{\text{equilibrium}} + \delta S'[F',\bar{\psi},\psi]$

$$\delta S'[F',\bar{\psi},\psi] \equiv \int d\tau\, F'(\tau)\, \hat{X}(\tau)$$

$$= \int d\tau\, F'(\tau) \sum_{aa'} \bar{\psi}_a(\tau) X_{aa'} \psi_{a'}(\tau)$$

With two generalized forces

$$S[F,F',\bar{\psi},\psi] \equiv S[F',\bar{\psi},\psi] + \delta S[F,\bar{\psi},\psi]$$

and $\mathcal{Z}[F,F'] \equiv \int d(\bar{\psi},\psi)\, e^{-S[F,F',\bar{\psi},\psi]}$

one has

$$X(\tau) = -\left.\frac{\delta}{\delta F(\tau)}\right|_{F=0} \ln \mathcal{Z}[F,F']$$

For $X(\tau) = \int d\tau'\, \underbrace{\chi(\tau,\tau')}_{\text{response function}}\, F'(\tau')$

this gives

$$\chi(T,T') = - \frac{\delta^2}{\delta F(T)\, \delta F'(T')}\bigg|_{F=F'=0} \ln Z[F,F']$$

and carrying out the derivatives

$$\boxed{\chi(T,T') = - Z^{-1} \frac{\delta^2}{\delta F(T)\, \delta F'(T')}\bigg|_{F=F'=0} Z[F,F']}$$

basic path integral
from which others
can be obtained via
<u>functional derivatives</u>