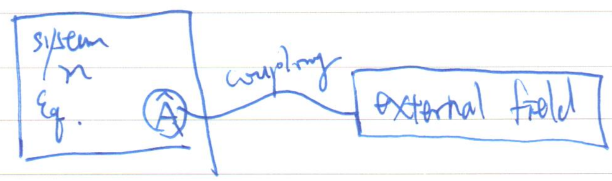
* response function formalism.

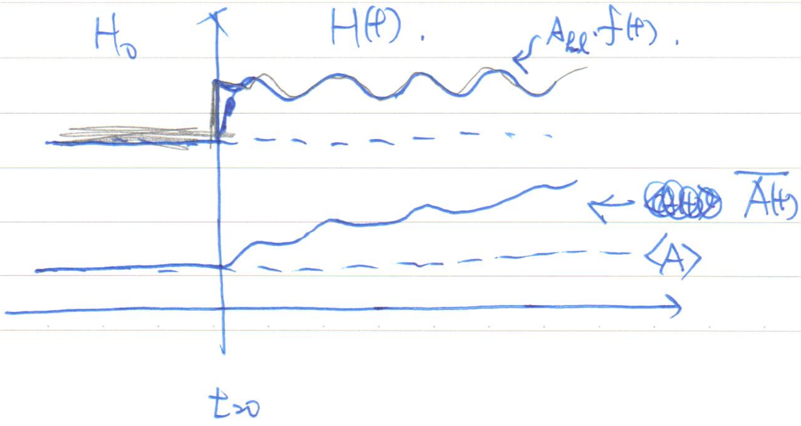
Now we come back to the original problem → to emphasize the effect of the external field, we consider a "initially equilibrium" system coupled to a external field:



$\hat{A}$: internal variable.

system operator

$$H(t) = H_0 - \hat{A} \cdot f(t)$$ ← external field



We want to calculate the response of the system :

$$\cancel{\langle A(t)\rangle - \langle A(t=0)\rangle}\,.\ \overline{A(t)} - \langle A\rangle$$

Note that the "ensemble average" $\langle\cdot\rangle$ has to be performed in order to obtain any useful information at finite temperature.

⇒ average over a thermal (Boltzmann distribution) distribution of initial states.

expectation value $\qquad A_I(t) = e^{\frac{iH_0 t}{\hbar}} \cdot A \cdot e^{-\frac{iH_0 t}{\hbar}}$

$$\cancel{\langle A(t)\rangle} \quad \langle A(t)\rangle = \langle \psi_I(t)|\, A_I(t)\, |\psi_I(t)\rangle$$

ensemble average $= \langle \psi(0)|\, U_I^\dagger(t) A_I(t)\, U_I(t)\, |\psi(0)\rangle$

$$\overline{A(t)} = \sum_n P_n \cdot \langle n|\, U_I^\dagger A_I\, U_I\, |n\rangle$$

$|n\rangle$ eigen states of H_0

Note that in 1^{st}-order TDPT :

$$U_I = 1 + \frac{i}{\hbar}\int_0^t f(\tau)\cdot A_I(\tau)\cdot d\tau\,.$$

Note that it is easy to extend to higher orders

$\therefore U_I^\dagger(t) \cdot A_I(t) U_I(t)$

$$\approx \left\{1 - \frac{i}{\hbar}\int_0^t A_I(\tau) f(\tau) . d\tau\right\} A_I(t) \left\{1 + \frac{i}{\hbar}\int_0^t A_I(\tau) f(\tau) d\tau\right\}$$

$$\approx A_I(t) + \frac{i}{\hbar}\int_0^t d\tau . f(\tau) . [A_I(t) A_I(\tau) - A_I(\tau) A_I(t)]$$

$$\therefore \overline{A(t)} = \overline{A_I(t)} + \frac{i}{\hbar}\int_0^t d\tau f(\tau) . \overline{[A_I(t), A_I(\tau)]}$$

Note $\overline{A_I(t)} = \sum_n P_n \cdot \langle n| e^{\frac{iH_0 t}{\hbar}} \cdot A \cdot e^{\frac{-iH_0 t}{\hbar}} |n\rangle$

$$= \sum_n P_n \langle n|A|n\rangle = \langle A \rangle$$

independence of t.

$\therefore$ ~~$\overline{A(t)} - \overline{A_I(t)} =$~~

also : $\overline{A_I(t') A_I(t'')} = \sum_n \langle n| e^{\frac{iH_0 t'}{\hbar}} \cdot A \cdot e^{\frac{-iH_0 t'}{\hbar}} \cdot e^{\frac{iH_0 t''}{\hbar}} \cdot A \cdot e^{\frac{-iH_0 t''}{\hbar}} |n\rangle$

$$= \sum_n \langle n| \underbrace{e^{\frac{iH_0(t'-t'')}{\hbar}} \cdot A \cdot e^{\frac{-iH_0(t'-t'')}{\hbar}}}_{A(t'-t'')} \cdot \underbrace{A}_{A(0)} |n\rangle$$

$$= \overline{A_I(t'-t'') A_I(0)}$$

this is actually a time correlation function :

If we define

Imp picture on H_0

$$C_{AA}(t) = \overline{A_I(t)\,A(0)} \equiv \langle A(t)\,A(0)\rangle$$

In fact $C_{AA}(t) = C^*_{AA}(-t)$

then response :

$$\overline{A(t)} - \langle A\rangle = \frac{i}{\hbar}\int_0^t d\tau \cdot f(\tau)\cdot\left[\langle A(t-\tau)A(0)\rangle - \langle A(0)A(t-\tau)\rangle\right]$$

$t-\tau \to \tau'$
extend to $-\infty \to t$.

now independent of "t".

$$= \frac{-i}{\hbar}\int_0^\infty d\tau' \underbrace{f(t-\tau')}_{\text{field}} \cdot \underbrace{\langle [A(\tau'), A(0)]\rangle}_{\text{material}} \cdot \theta(\tau')$$

t-dependence here !!

enforce "0" at $\tau' < 0$ (i.e. $t < \tau$).

Therefore, we can define linear response function :

$$R(\tau) = -\frac{i}{\hbar}\langle [A(\tau), A(0)]\rangle \cdot \theta(\tau).$$

Note that if $C_{AA}(t) = \underbrace{C'_{AA}(t)}_{\text{real}} + i\,\underbrace{C''_{AA}(t)}_{\text{imag}}$.

then $R(\tau) = \frac{-i}{\hbar}\theta(\tau)\cdot\{C_{AA}(\tau) - C_{AA}(-\tau)\}$

$$= \frac{2}{\hbar}\theta(\tau)\cdot C''_{AA}(\tau).$$

timeless

* properties of R

1. linear response $R(\tau)$ is real & related to imaginary part of TCF.
2. $R(\tau)=0$ if $\tau<0$ (Causality):

   The system can not response before the force has been applied.

* Response function & absorption spectrum.

Now we come back to light-matter interaction and consider energy absorption from an electromagnetic field.

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

Experimental measurement of absorption spectrum actually measures energy absorption over the ensemble:

assume stationary $\overline{A(t)}$
so $\frac{\partial}{\partial t}\overline{A(t)} = 0$.

$$\dot{E} = \frac{\partial \overline{H}}{\partial t} = -\frac{\partial f}{\partial t} \cdot \overline{A(t)}$$

average over a time period. (stationary).

$$= \frac{1}{T}\int_0^T dt \cdot \left[-\frac{\partial f}{\partial t} \cdot \overline{A(t)}\right]$$

$$= \frac{1}{T}\int_0^T dt \cdot \frac{\partial f(t)}{\partial t} \cdot \left[\langle A\rangle + \int_0^\infty d\tau\, R(\tau) \cdot f(t-\tau)\right]$$

because $f(t)$ is time dependent.

For a monochromatic field:

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

Therefore

$$\frac{1}{2}\int_0^\infty d\tau \cdot R(\tau) \cdot \left[E_0 \cdot e^{-i\omega(t-\tau)} + E_0^* \cdot e^{i\omega(t-\tau)}\right]$$

$$= \frac{1}{2}\left[E_0 \cdot \chi(\omega) \cdot e^{-i\omega t} + E_0^* \cdot \chi(-\omega) \cdot e^{i\omega t}\right].$$

where we have defined the

frequency-domain response.

susceptibility of the system:

$$\chi(\omega) = \int_0^\infty d\tau \cdot R(\tau) \cdot e^{i\omega\tau}.$$

We will come back to the properties of the susceptibility later. With the definition of $\chi(\omega)$, we can rewrite the energy absorption rate:

also $f(t) = -E_0 \sin\omega t$

$$\dot{E} = -\frac{1}{T}\langle A\rangle\left[f(T) - f(0)\right] - \frac{1}{4T}\int_0^T dt\left[-i\omega E_0 e^{-i\omega t} + i\omega E_0^* e^{i\omega t}\right]\cdot\left[E_0 e^{-i\omega t}\chi(\omega) + E_0^* e^{i\omega t}\chi(-\omega)\right]$$

Now we "cycle average" this expression, setting $T = \frac{2\pi}{\omega}$

$\Rightarrow$ rate of energy absorption from the field is

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

$$= \frac{\omega}{2}|E_0|^2\cdot\chi''(\omega).$$

$\leftarrow$ we will go back to $\chi''(\omega)$ later.

$\chi''(\omega)$ is the imaginary part of $\chi(\omega)$

$\therefore$ The absorption coefficient is

$$\alpha(\omega) = \frac{\dot{E}}{I} = \frac{4\pi\omega}{c}\cdot\chi''(\omega).$$

Thus, the absorption of energy from an external field (non-equilibrium response) depends on the imaginary part of $\chi(\omega)$,

$\Rightarrow$ $\chi(\omega)$ ~~describe~~ (or equivalently $R(\tau)$) describes non-equilibrium dynamics of a system.

Nontheless, $\chi(\omega) \leftarrow R(\tau)$ ~~depends~~ is related to the imaginary part of the time-correlation function.

$\Rightarrow$ $C_{AA}(\tau)$ describes equilibrium fluctuations of a system.

$\chi(\omega)$ & $\tilde{C}_{AA}(\omega)$ are related to each other

$\Rightarrow$ fluctuation – dissipation relationships.

* properties of $\chi(\omega)$.

The physical meaning of susceptibility is clear if we consider the Fourier transform of time-dependent response:

$$\widetilde{\delta A}(\omega) = \int_{-\infty}^{\infty} dt \cdot \widetilde{\delta A}(t)$$

$$\tilde{f}(\omega) = \int_{-\infty}^{\infty} d\tau \cdot e^{i\omega\tau} \cdot f(\tau).$$

$$= \tilde{f}(\omega) \cdot \chi(\omega) \quad \chi(\omega) = \int_0^{\infty} d\tau \cdot R(\tau) \cdot e^{i\omega t}.$$

$\Rightarrow$ $\chi(\omega)$ is the linear response of the system when driven by a field with frequency "ω".

$\Rightarrow$ what we are talking here is the "electric susceptibility"

In addition, with the definition

$$\chi(\omega) = \int_0^{\infty} d\tau \cdot R(\tau) \cdot e^{i\omega t}$$

$$= \underbrace{\int_0^{\infty} d\tau \cdot R(\tau) \cdot \cos(\omega t)}_{=\chi'(\omega)} + i \underbrace{\int_0^{\infty} d\tau \cdot R(\tau) \cdot \sin(\omega \tau)}_{=\chi''(\omega)}$$

$$= \chi'(\omega) + i \chi''(\omega).$$

It is clear that

$\chi'(\omega)$ is even in ω, $\chi''(\omega)$ is odd in ω.

moreover $\chi(-\omega) = \chi^*(\omega)$.

Therefore $\chi(-\omega) - \chi(\omega) = -2i\chi''(\omega)$.

* Kramers-Kröng relations

Note that the real part and the imaginary part of $\chi(\omega)$ are derived from the same function, therefore they are related to each other. ~~Krönig~~

Given $\chi'(\omega)$, $\chi''(\omega)$ (or effectively the whole $\chi(\omega)$) can be calculated and vice versa.

e.g.

inverse FT of $\chi(\omega)$

$$\chi'(\omega) = \frac{1}{\pi}\int_0^\infty dt \cos\omega t \cdot \int_{-\infty}^{\infty} \chi''(\omega') \cdot \sin\omega' t \cdot d\omega'$$

$$= \frac{1}{\pi}\lim_{L\to\infty}\int_{-\infty}^{\infty} d\omega' \chi''(\omega') \int_0^L \cos\omega t \cdot \sin\omega' t \cdot dt.$$

Using $\cos ax \sin bx = \frac{1}{2}[\sin(a+b)x + \sin(b-a)x]$

therefore

at $L\to\infty$ "$\omega \neq \omega'$"

principle value

a consequence of causality and the symmetric of response function!!

$$\chi'(\omega) = \frac{1}{\pi} \lim_{L\to\infty} \mathbb{P}\int_{-\infty}^{\infty} d\omega' \chi''(\omega') \times \frac{1}{2}\left[\frac{-\cos(\omega'+\omega)L+1}{\omega'+\omega} - \frac{\cos(\omega'-\omega)L+1}{\omega'-\omega}\right]$$

real axis without the pole.

this term survives as $L\to\infty$

$$\therefore\ \chi'(\omega) = \frac{1}{\pi}\mathbb{P}\int_{-\infty}^{\infty} \frac{\chi''(\omega')}{\omega'-\omega}\, d\omega'$$

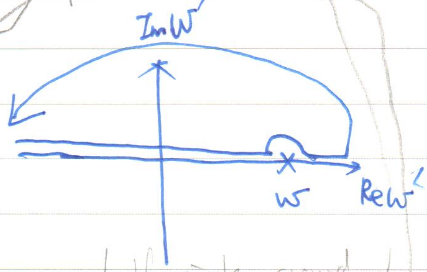
$$\chi''(\omega) = -\frac{1}{\pi}\mathbb{P}\int_{-\infty}^{\infty} \frac{\chi'(\omega')}{\omega'-\omega}\, d\omega'$$

These are the famous Kramers-Kronig relations.

this is actually a consequence of causality.

Another derivation:

Given that $\chi(\omega)$ is analytic, then along the path, the residue theorem yields:



half circle around the pole

$$\oint \frac{\chi(\omega')}{\omega'-\omega} d\omega' = 0 = \int_{-\infty}^{\infty} \frac{\chi(\omega')}{\omega'-\omega} d\omega' - i\pi\chi(\omega)$$

$$\therefore\ \chi(\omega) = \frac{1}{i\pi}\mathbb{P}\int_{-\infty}^{\infty} \frac{\chi(\omega')}{\omega'-\omega} d\omega'$$

timeless

* optical responses

Finally we emphasize the optical responses.

Note that $\hat{A} = \hat{\mu} \Rightarrow R(t) = \mathrm{Im}\cdot[C_{\mu\mu}(t)] \times \frac{2}{\hbar}\cdot\theta(t)$

optical response is derived by dipole-dipole TCF. The susceptibility

$$\chi(\omega) = \int_0^\infty d\tau \cdot \frac{2}{\hbar}\cdot \mathrm{Im}[C_{\mu\mu}(t)] \cdot e^{i\omega\tau}.$$

is the electric susceptibility. Actually $\chi(\omega)$ yields how the dipole of the molecular system is been ~~perturbated~~ modulated by EM field:

Frequency-dependent polarization: $(P(t) = \mathrm{Tr}\,\mu\rho(t) \equiv \langle\mu\rho(t)\rangle)$

electric permittivity of free space

$$\therefore\ P(\omega) = \overline{\delta\mu(\omega)} = \varepsilon_0 \cdot \chi(\omega).E(\omega).$$

Electric displacement: $D = \varepsilon_0 E + P$

frequency dependent

$$= \varepsilon_0\,(1+\chi_e).\,E$$

dielectric constant of material.

$$= \varepsilon_0 \cdot \varepsilon_r(\omega).\,E(\omega)$$

Now we can ~~couple~~ connect the quantum electric susceptibility to marcoscopic optics!!

$$\varepsilon_r(\omega) = 1 + \chi(\omega)$$
$$= 1 + \chi'(\omega) + i\chi''(\omega)$$

If we define a complex index of refraction

(real) refractive index.

$$n = \eta + i\kappa$$

extinction coefficient. (cause dispersion of EM field)

In a dielectric, EM field

$\mu_r \approx 1$

$n = \sqrt{\varepsilon_r \mu_r}$

$\approx \sqrt{\varepsilon_r}$

$$k = \frac{n\omega}{c}$$

and $\varepsilon_r \approx n^2 = \underbrace{(\eta^2 - \kappa^2)}_{1+\chi'(\omega)} + \underbrace{2\eta\kappa \cdot i}_{\chi''(\omega)}$.

Beer's law:

$$K = \frac{2\omega\kappa}{2}$$

Beer's law absorption coefficient.