(Third order) response functions in cumulant approximation

Let us start with the 1. order response function

$$J_1(t) = Tr\left\{ U^{+}(t)\hat{\mu}\, U(t)\hat{\mu}\,\rho(-\infty) \right\} =$$

$$= Tr_Q\left\{ \langle g| U_g^{+}(t) |g\rangle \langle g| d |g\rangle \langle e| U_e(t) |e\rangle \langle e| d |e\rangle \langle g|\rho_{eq}|g\rangle \right\}$$

$$= |d|^2\, Tr_Q\left\{ \tilde{U}_g^{+}(t)\, \tilde{U}_e(t)\, \rho_{eq} \right\} e^{-i\omega_{eg} t}$$

$$\tilde{U}_g(t) = \exp\left\{ -\frac{i}{\hbar} H_B t \right\}$$

$$\tilde{U}_e(t) = \exp\left\{ -\frac{i}{\hbar} H_B t - \frac{i}{\hbar}\Delta V t \right\}$$

if we could write $\tilde{U}_e(t)$ as $\exp\left\{-\frac{i}{\hbar} H_B t\right\} \cdot \bar{U}_e(t)$ the problem might simplify. Can we do that?

H_B and ΔV do not commute, so it cannot be split like $\tilde{U}_e(t) \neq \exp\left\{-\frac{i}{\hbar} H_B t\right\} \exp\left\{-\frac{i}{\hbar}\Delta V t\right\}$

We know that the evolution operator satisfies the Schrödinger eq.

$$\frac{\partial}{\partial t}\tilde{U}_e(t) = -\frac{i}{\hbar}\left[H_B + \Delta V\right]\tilde{U}_e(t)$$

go into interaction picture

$$\tilde{U}_e^{(I)}(t) = \exp\left\{\frac{i}{\hbar}H_B t\right\}\tilde{U}_e(t) \Rightarrow \tilde{U}_e(t) = \exp\left\{-\frac{i}{\hbar}H_B t\right\}\tilde{U}_e^{(I)}(t)$$

This is what we need

$$\frac{\partial}{\partial t}\tilde{U}_e^{(I)}(t) = \frac{i}{\hbar}H_B \exp\left\{\frac{i}{\hbar}H_B t\right\}\tilde{U}_e(t)$$

$$+ \exp\left\{\frac{i}{\hbar}H_B t\right\}\frac{\partial}{\partial t}\tilde{U}_e(t) = \frac{i}{\hbar}\exp\left\{\frac{i}{\hbar}H_B t\right\}H_B\tilde{U}_e(t) - \frac{i}{\hbar}\exp\left\{\frac{i}{\hbar}H_B t\right\}$$

$$\times H_B\tilde{U}_e(t) - \frac{i}{\hbar}\exp\left\{\frac{i}{\hbar}H_B t\right\}\Delta V\,\tilde{U}_e(t)$$

$$\frac{\partial}{\partial t}\tilde{U}_e^{(I)}(t) = -\frac{i}{\hbar}\underbrace{\exp\left\{\frac{i}{\hbar}H_B t\right\}\Delta V\exp\left\{-\frac{i}{\hbar}H_B t\right\}}_{\Delta V(t)}\tilde{U}_e^{(I)}(t)$$

$$\Rightarrow \boxed{\tilde{U}_e^{(I)}(t) = \exp\left\{-\frac{i}{\hbar}\int_0^t U_B^+(\tau)\,\Delta V\,U_B(\tau)\,d\tau\right\}}$$

Putting everything together we see that

$$\boxed{\tilde{U}_g^+(t)\,\tilde{U}_e(t) = \exp\left\{-\frac{i}{\hbar}\int_0^t d\tau\, U_B^+(\tau)\,\Delta V\,U_B(\tau)\right\}}$$

It yields

$$\boxed{J_1(t) = |d|^2\, Tr_Q\left\{\exp\left\{-\frac{i}{\hbar}\int_0^t d\tau\, U_B^+(\tau)\,\Delta V\,U_B(\tau)\right\}\rho_{eq}\right\}e^{-i\omega_{eg}t}} \qquad (\;\;)$$

We have an exp, which could be expanded, but there is a better way

Lets have an „operator" or function, which we expand in ~~...~~ small parameter λ

$$A = A_0(1 + \lambda A_1 + \lambda^2 A_2 + \dots)$$

But our function looks like an exponentional so why not to take an ansatz

$$A = A_0 \exp(F)$$

and make an expansion $F = \lambda F_1 + \lambda^2 F_2 + \dots$

$$\exp(\lambda F_1 + \lambda^2 F_2 + \dots) = 1 + (\lambda F_1 + \lambda^2 F_2 + \dots) + \frac{1}{2}(\lambda F_1 + \lambda^2 F_2 + \dots)^2$$

We compare the two expansions order by order

$$F_1 = A_1$$

$$A_2 = F_2 + \frac{1}{2} F_1^2 = F_2 = A_2 - \frac{1}{2} A_1^2$$

It means that knowing Taylor expansion we can construct the better expansion up to the second order

$$A \doteq A_0 \exp\left\{ A_1 \lambda + (A_2 - \tfrac{1}{2} A_1^2)\lambda^2 \right\}$$

Let us apply this to Eq. ( )

$$\mathrm{Tr}_Q\left\{ \exp_+\left\{-\frac{i}{\hbar}\int_0^t d\tau\, \Delta V(\tau)\right\}\rho_{eq}\right\} = 1 - \frac{i}{\hbar}\int_0^t d\tau\, \mathrm{Tr}_Q\left\{U_B^+(\tau)\,\Delta V\, U_B(\tau)\,\rho_{eq}\right\}$$

$$+\left(\frac{i}{\hbar}\right)^2 \int_0^t d\tau \int_0^\tau d\tau'\, \mathrm{Tr}_Q\left\{\Delta V(\tau)\,\Delta V(\tau')\,\rho_{eq}\right\} + \dots$$

1. order term

$$Tr_Q\{U_B^+(\tau)\,\Delta V\,U_B(\tau)\rho_{eq}\} = Tr_Q\{\Delta V\,U_B(\tau)\rho_{eq}U_B^+(\tau)\} =$$

$$= Tr_Q\{\Delta V\rho_{eq}\} = Tr_Q\{\left(V_e(Q)-V_g(Q) - Tr_Q\{V_e(Q)-V_g(Q)\}\right)\rho_{eq}\}$$

$U_B(\tau)\rho_{eq}U_B^+(\tau) = \rho_{eq}$ $\leftarrow$ now evolution for the equilibrium

$$= Tr_Q\{(V_e(Q)-V_g(Q))\rho_{eq}\} - Tr_Q\{(V_e(Q)-V_g(Q))\rho_{eq}\} = 0$$

2. order term

$$-\frac{1}{\hbar^2}\int_0^t d\tau\int_0^\tau d\tau'\; Tr_Q\{U_B^+(\tau)\,\Delta V\,U_B(\tau-\tau')\,\Delta V\,U_B(\tau')\rho_{eq}\} =$$

$$= -\frac{1}{\hbar^2}\int_0^t d\tau\int_0^\tau d\tau'\; Tr_Q\{U_B^+(\tau-\tau')\,\Delta V\,U_B(\tau-\tau')\,\Delta V\rho_{eq}\}$$

$$\tau'' = \tau-\tau' \quad ; \; \tau''(\tau) = 0$$
$$d\tau'' = -d\tau' \quad \tau''(0) = \tau$$

$$= -\frac{1}{\hbar^2}\int_0^t d\tau\int_0^\tau d\tau''\; Tr_Q\{U_B^+(\tau'')\,\Delta V\,U_B(\tau'')\,\Delta V\rho_{eq}\}$$

We define <u>correlation function</u>

$$\boxed{C(t) = \frac{1}{\hbar^2}\,Tr_Q\{U_B^+(t)\,\Delta V\,U_B(t)\,\Delta V\rho_{eq}\}}$$

and so-called <u>line shape function</u>

$$\boxed{g(t) = \int_0^t d\tau\int_0^\tau d\tau'\,C(\tau')}$$

$Tr_Q\{\dots\} \approx$

$\approx 1 - g(t) \approx e^{-g(t)}$

Putting all together

$$J_1(t) = |d|^2 e^{-g(t)} e^{-i\omega_{eg}t}$$

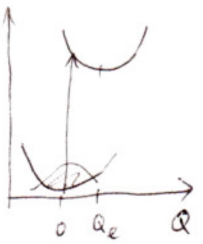
and writing the expression for linear absorption we get

$$H_a(\omega) = \frac{4\pi\omega}{n(\omega)c\hbar}|d|^2 \mathrm{Re}\int_0^\infty dt\left[e^{-g(t)-i(\omega_{eg}-\omega)t} - e^{-g^*(t)+i(\omega_{eg}+\omega)t}\right]$$

$$\approx \frac{4\pi\omega}{n(\omega)c\hbar}|d|^2 \mathrm{Re}\int_0^\infty dt\, e^{-g(t)-i(\omega_{eg}-\omega)t}$$

<u>Some comments on $g(t)$</u>

$$C(t) = \frac{1}{\hbar^2}\langle U_B^+(t)\Delta V U_B(t)\Delta V \rho_{eq}\rangle$$



$$\Delta V = \frac{1}{2}\varepsilon(Q-Q_e)^2 - \frac{1}{2}\varepsilon Q^2 - \langle\ldots\rangle =$$

$$= \cancel{\frac{1}{2}\varepsilon Q^2} - \frac{2}{2}\varepsilon Q Q_e + \frac{1}{2}\varepsilon Q_e^2 - \cancel{\frac{1}{2}\varepsilon Q^2} - \langle\ldots\rangle$$

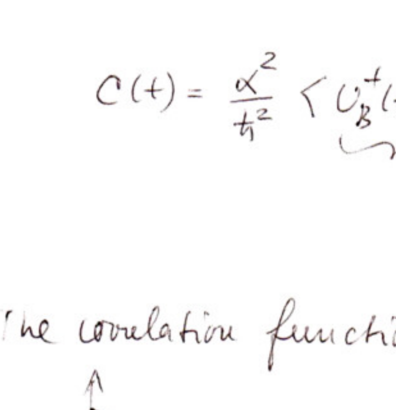
$\langle Q\rangle = 0$

$$= \varepsilon Q Q_e + \frac{1}{2}\varepsilon Q_e^2 - \underbrace{\langle\ldots\rangle}_{=\frac{1}{2}\varepsilon Q_e^2} = \varepsilon Q_e Q \equiv \alpha Q$$

$$C(t) = \frac{\alpha^2}{\hbar^2}\langle \underbrace{U_B^+(t) Q U_B(t)}_{Q(t)} Q \rho_{eq}\rangle \approx \frac{\alpha^2}{\hbar^2}\langle Q(t)Q(0)\rho_{eq}\rangle$$

evolving Heisenberg operator

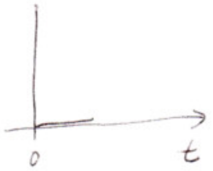
The correlation function looks like this



We might consider two limits → fast
↘ slow dynamics

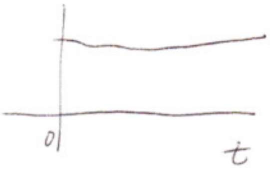
Fast

$$C(t) \approx \Gamma \delta(t)$$



Slow

$$C(t) \approx \Delta$$



as a result

$$g(t) = \Gamma \int_0^t d\tau \int_0^\tau d\tau' \, \delta(\tau') = \Gamma t$$

$$g(t) = \Delta \int_0^t d\tau \int_0^\tau d\tau' = \frac{1}{2} \Delta t^2$$

$$\mathrm{Re} \int_0^\infty dt \, A(t) e^{i\omega t} = \int_0^\infty dt \, A(t) e^{i\omega t} + \int_0^\infty dt \, A^*(t) e^{-i\omega t} =$$

$$= \int_0^\infty dt \, A(t) e^{i\omega t} + \int_0^{-\infty} dt' \, A^*(-t') e^{+i\omega t'}$$

$$= \int_0^\infty dt \, A(t) e^{i\omega t} + \int_{-\infty}^0 dt' \, A(t') e^{i\omega t'} = \int_{-\infty}^\infty dt' \, A(t) e^{i\omega t'}$$

Fast

$$\mathcal{H}_a(\omega) \approx \mathrm{Re} \frac{1}{-\Gamma - i(\omega - \omega_{eg})} \left[0 - 1 \right] =$$

$$= \mathrm{Re} \left(\frac{1}{\Gamma + i(\omega - \omega_{eg})} \right) = \frac{\Gamma}{\Gamma^2 - (\omega - \omega_{eg})^2}$$ Lorentz line shape

Slow $$\mathcal{H}_a(\omega) \approx e^{-\frac{(\omega - \omega_{eg})^2}{6}}$$ Gauss line shape

Could we do something like this for 3. order?

Let us try $\bar{R}_3(t_3, t_2, t_1)$

$$\mathrm{Tr}_Q\left\{ \tilde{U}_e^+(t_1)\tilde{U}_g^+(t_2+t_3)\tilde{U}_e(t_3)\tilde{U}_g(t_1+t_2)\rho_{eq}\right\} =$$

$$= \mathrm{Tr}_Q\left\{ \underbrace{U_e^+(t_1)U_g(t_1)}\, U_g^+\underbrace{(t_1+t_2+t_3)\, U_e(t_1+t_2+t_3)}\, U_e^+\underbrace{(t_1+t_2)\, U_g}(t_1+t_2)\rho_{eq}\right\}$$

In addition to what we have, we need to derive

$$U_e^+(t)U_g(t) = \exp_-\left\{ +\frac{i}{\hbar}\int_0^t d\tau\, U_B^+(\tau)\Delta V U_B(\tau)\right\}$$

$$\bar{R}_3(t_3,t_2,t_1) = \mathrm{Tr}_Q\left\{ \exp_-\left\{\frac{i}{\hbar}\int_0^{t_1} d\tau\, U_B^+(\tau)\Delta V U_B(\tau)\right\} \exp_+\left\{-\frac{i}{\hbar}\int_0^{t_1+t_2+t_3} d\tau\, U_B^+(\tau)\Delta V U_B(\tau)\right\}\right.$$

$$\left.\times \exp_-\left\{\frac{i}{\hbar}\int_0^{t_1+t_2} d\tau\, \Delta V(\tau)\right\}\rho_{eq}\right\}$$

$$= \mathrm{Tr}_Q\left\{ \left(1 + \frac{i}{\hbar}\int_0^{t_1} d\tau \Delta V(\tau) - \frac{1}{\hbar^2}\int_0^{t_1} d\tau \int_0^{\tau} d\tau' \Delta V(\tau')\Delta V(\tau)\right)\right.$$

$$\times\left(1 - \frac{i}{\hbar}\int_0^{t_1+t_2+t_3} d\tau\, \Delta V(\tau) - \frac{1}{\hbar^2}\int_0^{t_1+t_2+t_3} d\tau \int_0^{\tau} d\tau' \Delta V(\tau)\Delta V(\tau')\right)$$

$$\left.\times\left(1 + \frac{i}{\hbar}\int_0^{t_1+t_2} d\tau\, \Delta V(\tau) - \frac{1}{\hbar^2}\int_0^{t_1+t_2} d\tau \int_0^{\tau} d\tau' \Delta V(\tau')\Delta V(\tau)\right)\rho_{eq}\right\}$$

$$= 1 - g_-(t_1) - g(t_1+t_2+t_3) - g_-(t_1+t_2)$$

$$+ h(t_1, t_1+t_2+t_3) - h(t_1, t_1+t_2) + h(t_1+t_2+t_3, t_1+t_2)$$

$$h(t_1,t_2) = \frac{1}{t_1^2}\int_0^{t_1} d\tau \int_0^{t_2} d\tau' \langle \Delta V(\tau)\Delta V(\tau')\rho_{eq}\rangle$$

Can we turn this into ordinary $g(t)$?

$$g_-(t) = \frac{1}{t_1^2}\int_0^{t} d\tau \int_0^{\tau} d\tau' \langle \Delta V(\tau')\Delta V(\tau)\rho_{eq}\rangle$$

To treat g_- is simpler

$$C_-(t) = \langle U_B^+(\tau')\Delta V U_B(\tau'-\tau)\Delta V U_B(\tau)\rho_{eq}\rangle = \langle \Delta V U_B(\tau'-\tau)\Delta V U_B^+(\tau'-\tau)\rho_{eq}\rangle$$

$$= \langle U_B(\tau-\tau')\Delta V U_B^+(\tau-\tau')\Delta V\rho_{eq}\rangle = \langle \rho_{eq}\Delta V U_B(\tau-\tau')\Delta V U_B^+(\tau-\tau')\rangle^*$$

$$= \langle U_B^+(\tau-\tau')\Delta V U_B(\tau-\tau')\Delta V\rho_{eq}\rangle^* \quad ; \quad C_-(t) = C(-t) = C^*(t)$$

$$\Rightarrow g_-(t) = g^*(t) = g(-t)$$

h can also be turned into g's

$$h(t_1,t_2) = \frac{1}{t_1^2}\int_0^{t_1} d\tau \int_0^{t_2} d\tau' \langle \Delta V(\tau)\Delta V(\tau')\rho_{eq}\rangle = \overbrace{\frac{1}{t_1^2}\int_0^{t_1} d\tau \int_0^{\tau} d\tau' \langle \Delta V(\tau)\Delta V(\tau')\rho_{eq}\rangle}^{g(t_1)}$$

$$+ \frac{1}{t_1^2}\int_0^{t_1} d\tau \int_{\tau}^{t_2} d\tau' \langle \Delta V(\tau)\Delta V(\tau')\rho_{eq}\rangle = g(t_1) + \frac{1}{t_1^2}\int_0^{t_1} d\tau \int_{\tau-t_2}^{0} dz \langle \Delta V(\tau)\Delta V(z+t_2)\rho_{eq}\rangle$$

$z = \tau' - t_2 \quad ; \tau' = z + t_2$

$dz = d\tau'$

$z(t_1) = \tau - t_2$

$z(t_2) = 0$

$$= g(t_1) - \frac{1}{t_1^2}\int_0^{t_1} d\tau \int_0^{\tau-t_2} dz \langle \Delta V(\tau)\Delta V(z+t_2)\rho_{eq}\rangle = g(t_1)$$

$y = \tau - t_2$

$dy = d\tau$

$y(0) = -t_2$

$y(t_1) = t_1 - t_2$

$$- \frac{1}{t_1^2}\int_{-t_2}^{t_1-t_2} dy \int_0^{y} dz \langle \Delta V(y+t_2)\Delta V(z+t_2)\rho_{eq}\rangle$$

$$= g(t_1) - g(t_1-t_2) + g(-t_2)$$

Using this result everything is now turned into g

$$\bar{R}_3(t_3,t_2,t_1) \approx 1 - g^*(t_1) - \cancel{g(t_1+t_2+t_3)} - g^*(t_1+t_2)$$

$$+ \cancel{g(t_1)} - g(-t_2-t_3) + g(-t_1-t_2-t_3) - \cancel{g(t_1)} + g^*(t_3) - g^*(t_1+t_2)$$

$$+ \cancel{g(t_1+t_2+t_3)} - g(t_3) + g^*(t_1+t_2)$$

$$\approx e^{-g^*(t_1) - g^*(t_1+t_2) + g^*(t_1+t_2+t_3) - g^*(t_2+t_3) + g(t_1-t_2-t_1) + g^*(t_2+t_3) - g(t_3)}$$

$$= e^{-g^*(t_1) - g(t_3) - g^*(t_1+t_2) + g^*(t_1+t_2+t_3) - g^*(t_2+t_3) + g^*(t_2)}$$

The same can be done with all pathways

$$\boxed{\begin{aligned}
\bar{R}_1(t_3,t_2,t_1) &= e^{-g^*(t_3) - g(t_1) - f_+(t_3,t_2,t_1)} \\
\bar{R}_2(t_3,t_2,t_1) &= e^{-g^*(t_3) - g^*(t_1) + f_+^*(t_3,t_2,t_1)} \\
\bar{R}_3(t_3,t_2,t_1) &= e^{-g(t_3) - g^*(t_1) + f_-^*(t_3,t_2,t_1)} \\
\bar{R}_4(t_3,t_2,t_1) &= e^{-g(t_3) - g(t_1) - f_-(t_3,t_2,t_1)} \\
f_-(t_3,t_2,t_1) &= g(t_2) - g(t_2+t_3) - g(t_1+t_2) + g(t_1+t_2+t_3) \\
f_+(t_3,t_2,t_1) &= g^*(t_2) - g^*(t_2+t_3) - g(t_1+t_2) + g(t_1+t_2+t_3)
\end{aligned}}$$

Now everything depends on the actual properties of the $g(t)$ or consequently the $C(t)$ functions.