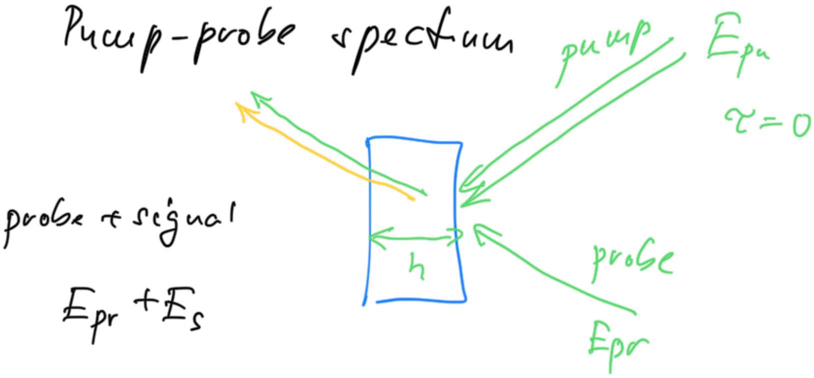
Constructing spectroscopy with simultaneous time and frequency resolutions

Pump-probe spectrum



$\Leftarrow$ 4-wave mixing

$$E_{out}(t) = E_{pr}(t) + \underline{E_s(t)}$$

$$E_s(t) \sim i\omega P(t) h$$

Frequency resolved detection $\longrightarrow$ we detect <u>Fourier components</u>

$$E_{out}(\omega) = E_{pr}(\omega) + E_s(\omega)$$

$$E_{out}(\omega) = E_{pr}(\omega) + \varkappa i \omega P(\omega) h$$

We assumed $\quad P^{(3)}(\omega) = \varepsilon_0 \tilde{\chi}(\omega) E_{pr}(\omega)$

"susceptibility" depends on E_{pu}^2

Detection of signal

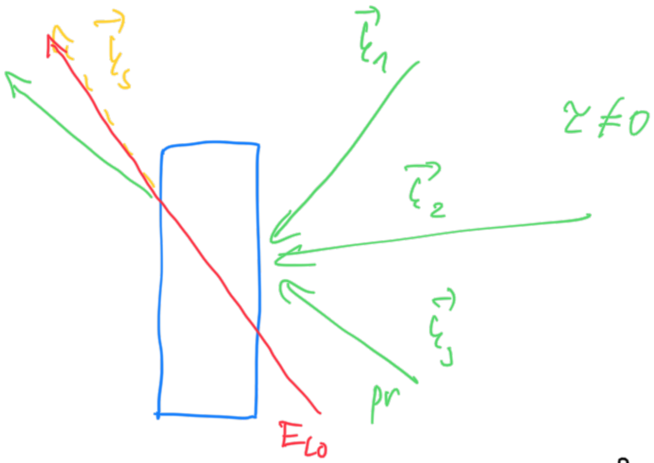
$$|E_{out}(\omega)|^2 = |E_{pr}(\omega)|^2 + 2\,\mathrm{Re}\, \underline{E_{pr}^*(\omega)}\, \varkappa i \omega \varepsilon_0 \tilde{\chi}(\omega) \underline{E_{pr}(\omega)}$$

$$+ \underbrace{\ldots}_{\text{small}}$$

$$\frac{|E_{out}(\omega)|^2 - |E_{pr}(\omega)|^2}{|E_{pr}(\omega)|^2} = \frac{2\,\mathrm{Re}\,\kappa\, i\omega\varepsilon_0\, \tilde{\chi}(\omega)\, \cancel{|E_{pr}(\omega)|^2}}{\cancel{|E_{pr}(\omega)|^2}}$$

in pump-probe we detect $\tilde{\chi}(\omega)$

More general signal generation (background free)



We can directly detect $|E_S(\omega)|^2$. Can we detect $E_S(\omega)$ or $\tilde{\chi}(\omega)$?

We add the „local oscillator" $E_{LO}(\omega)$

$$E_{tot}(\omega) = E_{LO}(\omega) + E_S(\omega)$$

$$|E_{tot}(\omega)|^2 = |E_{LO}(\omega)|^2 + 2\,\mathrm{Re}\, E_{LO}^*(\omega) E_S(\omega) + \ldots$$

$$\mathrm{sig}(\omega) = \frac{|E_{tot}(\omega)|^2 - |E_{LO}(\omega)|^2}{|E_{LO}(\omega)|^2} = \frac{2\,\mathrm{Re}\, E_{LO}^*(\omega) E_S(\omega)}{|E_{LO}(\omega)|^2}$$

$$\boxed{\propto E_{LO}(\omega) e^{i\phi} = E_{pr}(\omega)}$$

$$E_S(\omega) = i\omega\, ӕ\, \tilde{\chi}(\omega)\, E_{pr}(\omega)$$

$$\mathrm{sig}(\omega) = \frac{2\,\mathrm{Re}\, \alpha\, \cancel{|E_{LO}(\omega)|^2}\, i\omega\, ӕ\, \tilde{\chi}(\omega)\, e^{i\phi}}{\cancel{|E_{LO}(\omega)|^2}}$$

We detect $\mathrm{Im}\, \tilde{\chi}(\omega)$ up to a phase factor $e^{i\phi}$!

This issue can be solved! We will do it later.

⇑ HETERODYNE DETECTION ⇑

What is $\tilde{\chi}(\omega)$?

$$P^{(3)}(t; T, \tau) = \int_0^\infty d\tau_3 \int_0^\infty d\tau_2 \int_0^\infty d\tau_1\, S^{(3)}(\tau_3, \tau_2, \tau_1) E(t-\tau_3) E(t-\tau_3-\tau_2) \times E(t-\tau_3-\tau_2-\tau_1)$$

$$E(t) = \underset{\substack{\approx e^{-i\omega t} \\ \vec{k}}}{E^{(+)}(t)} + \underset{\substack{\approx e^{+i\omega t} \\ -\vec{k}}}{E^{(-)}(t)}$$

$$S^{(3)}(\tau_3, \tau_2, \tau_1) \overset{\text{redef.}}{\Longrightarrow} \Theta(\tau_3)\Theta(\tau_2)\Theta(\tau_1)\, S^{(3)}(\tau_3, \tau_2, \tau_1)$$

Components of the polarization → using Fourier transforms

$-\vec{k}_1$

$$E^{(-)}(t-\tau_3-\tau_2-\tau_1) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega_1\, e^{i\omega_1(t-\tau_3-\tau_2-\tau_1)} E^{(-)}(\omega_1)$$

distribution of frequencies in the pulse

$+\vec{k}_1$

$$E^{(+)}(t-\tau_3-\tau_2-\tau_1) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\omega_1\, e^{-i\omega_1(t-\tau_3-\tau_2-\tau_1)} E^{(+)}(\omega_1)$$

$\omega_1 \approx \omega$

central pulse frequency

$$P^{(3)}(t) = \int_{-\infty}^{\infty} d\tau_3 \int_{-\infty}^{\infty} d\tau_2\, E(t-\tau_3) E(t-\tau_3-\tau_2) \int_{-\infty}^{\infty} d\tau_1\, S(\tau_3,\tau_2,\tau_1)\, E(\underbrace{t-\tau_3-\tau_2}_{t}-\tau_1)$$

$$= \int_{-\infty}^{\infty} d\tau_3 \int_{-\infty}^{\infty} d\tau_2\, E(t-\tau_3) E(t-\tau_3-\tau_2) \times$$

$\sim e^{+i\omega_a(\tau_3-\tau_1)}$ $\quad -\vec{k}_1 + \vec{k}_2 + \vec{k}_3 \rightarrow 1-2-3$

$$\times \left(\int_{-\infty}^{\infty} d\tau_1\, S_R(\tau_3,\tau_2,\tau_1) E^{(-)}(t-\tau_1) \right.$$

I.

II.

$$\left. + \int_{-\infty}^{\infty} d\tau_1\, S_{NR}(\tau_3,\tau_2,\tau_1) E^{(+)}(t-\tau_1) \right)$$

$\vec{k}_2 - \vec{k}_1 + \vec{k}_3 \rightarrow 2-1-3$

$$\int_{-\infty}^{\infty} d\tau_1\, S_R(\tau_3,\tau_2,\tau_1) \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi}\, e^{i\omega_1(t-\tau_1)} E^{(-)}(\omega_1) =$$

$$= \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \left[\int_{-\infty}^{\infty} d\tau_1\, S_R(\tau_3,\tau_2,\tau_1)\, e^{-i\omega_1\tau_1} \right] e^{i\omega_1 t} E^{(-)}(\omega_1)$$

$$= \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi}\, S_R(\tau_3,\tau_2,\underline{\omega_1}) E^{(-)}(\omega_1)\, e^{i\omega_1(t-\tau_3-\tau_2)}$$

II.

$$\int_{-\infty}^{\infty} d\tau_1\, S_{NR}(\tau_3, \tau_2, \tau_1) \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi}\, e^{-i\omega_1(t-\tau_1)} E^{(+)}(\omega_1) =$$

$$= \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi}\, S_{NR}(\tau_3, \tau_2, \omega_1) E^{(+)}(\omega_1)\, e^{-i\omega_1(t-\tau_3-\tau_2)}$$

$+i\omega\tau_2$

$-i\omega(t-\tau_3-\tau_2)$

$\sim e$

$-i\omega_1\tau_2$

$$\boxed{P^{(3)}(t)} = \int_{-\infty}^{\infty} d\tau_3 \int_{-\infty}^{\infty} d\tau_2\, E(t-\tau_3) E^{(+)}(t-\tau_3-\tau_2) \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi}\, S_R(\tau_3, \tau_2, \omega_1) E^{(-)}(\omega_1)\, e^{i\omega_1(t-\tau_3-\tau_2)}$$

$$+ \int_{-\infty}^{\infty} d\tau_3 \int_{-\infty}^{\infty} d\tau_2\, E(t-\tau_3) E^{(-)}(t-\tau_3-\tau_2) \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi}\, S_{NR}(\tau_3, \tau_2, \omega_1) E^{(+)}(\omega_1)\, e^{-i\omega_1(t-\tau_3-\tau_2)}$$

$$= \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega_2}{2\pi} \int_{-\infty}^{\infty} d\tau_3\, E(t-\tau_3)\, S_R(\tau_3, \omega_1-\omega_2, \omega_1) E^{(+)}(\omega_2) E^{(-)}(\omega_1) \times e^{i(\omega_1-\omega_2)(t-\tau_3)}$$

$$E^{(+)} \sim \int d\omega_2\, e^{-i\omega_2(t-\tau_3-\tau_2)} \approx e^{+i\omega_2\tau_2}$$

$+ \dots$

$$= \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega_2}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega_3}{2\pi}\, S_R(\omega_3-\omega_1+\omega_2, \omega_1-\omega_2, \omega_1) E^{(+)}(\omega_3) E^{(+)}(\omega_2) E^{(-)}(\omega_1) \times e^{-i(\omega_3+\omega_2-\omega_1)t}$$

$$+ \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega_2}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega_3}{2\pi}\, S_{NR}(\omega_3+\omega_1-\omega_2, \omega_2-\omega_1, \omega_1) E^{(+)}(\omega_3) E^{(-)}(\omega_2) E^{(+)}(\omega_1) \times e^{-i(\omega_3-\omega_2+\omega_1)t}$$

$$P^{(3)}(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t}\, P^{(3)}(t)$$

$$= \int_{-\infty}^{\infty} dt \int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_2}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_3}{2\pi}\Bigg(\Big[S_R(\dots)E^{(+)}E^{(+)}E^{(-)}\Big]\, e^{i[\omega-(\omega_3+\omega_2-\omega_1)]t}$$

$\delta(\omega-(\omega_3+\omega_2-\omega_1))$

$$+\Big[S_{NR}(\dots)E^{(+)}E^{(-)}E^{(+)}\Big]\, e^{i[\omega-(\omega_3-\omega_2+\omega_1)]t}$$

$\delta(\omega-(\omega_3-\omega_2+\omega_1))$

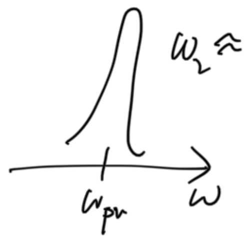
$$\boxed{\begin{aligned} P^{(3)}(\omega) = \int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_2}{2\pi}\; & S_R(\omega, \omega_1-\omega_2, \omega_1)\, E^{(+)}(\omega_2)\, E^{(-)}(\omega_1)\, E^{(+)}(\omega-\omega_2+\omega_1) \\ & + S_{NR}(\omega, \omega_2-\omega_1, \omega_1)\, E^{(+)}(\omega_1)\, E^{(-)}(\omega_2)\, E^{(+)}(\omega-\omega_1+\omega_2) \end{aligned}}$$

? $P^{(3)}(\omega) = \tilde{\chi}(\omega) E_{pr}(\omega)$?

Narrow pulses (in ω)

$\omega_2 \approx \omega_{pu} \equiv$ pump frequency

$\omega_1 \approx \omega_{pu}$



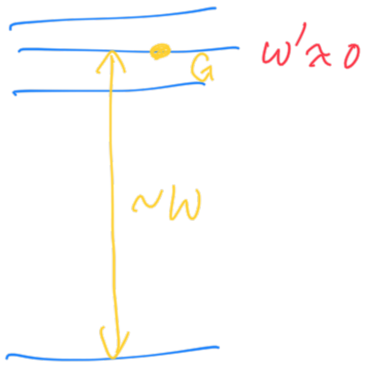
$\omega_2 \approx \omega_{pu} \approx \omega_1$

$$\Rightarrow E^{(+)}(\omega-\omega_1+\omega_2) \approx E^{(+)}(\omega)$$

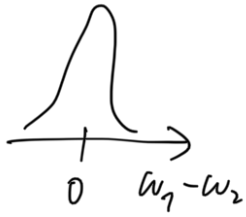
$$\boxed{P^{(3)}(\omega) \approx \tilde{\chi}(\omega) E^{(+)}(\omega)}$$

Properties of S_R and S_{NR}

$$S_R(\tau_3,\tau_2,\tau_1) \approx \underbrace{\mathcal{U}_{mgmg}(\tau_3)}_{\sim e^{-i\omega_{mg}\tau_3}}\,\mathcal{U}(\tau_2)\,\underbrace{\mathcal{U}_{gmgm}(\tau_1)}_{e^{i\omega_{mg}\tau_1}}$$



$$S_R(\dots,\omega_1-\omega_2,\dots) \approx$$



enforces $\omega_1 \approx \omega_2$

$$\Rightarrow \quad E^{(+)}(\omega-\omega_2+\omega_1) \approx E^{(+)}(\omega-\omega_1+\omega_2) \approx E^{(+)}(\omega)$$

The form

$$\boxed{P^{(3)}(\omega) = \tilde{\chi}(\omega)\,E^{(+)}(\omega)}$$

is valid

$$\boxed{\begin{aligned}\tilde{\chi}(\omega) = \int_{-\infty}^{\infty}\frac{d\omega_1}{2\pi}\int_{-\infty}^{\infty}\frac{d\omega_2}{2\pi}\Big[&S_R(\omega,\omega_1-\omega_2,\omega_1)\,E^{(+)}(\omega_2)\,E^{(-)}(\omega_1)\\ &+S_{NR}(\omega,\omega_2-\omega_1,\omega_1)\,E^{(+)}(\omega_1)\,E^{(-)}(\omega_2)\Big]\end{aligned}}$$

$$\equiv \tilde{\chi}(\omega;T,\tau)$$

Time dependent signal

$$\mathrm{sig}(t) = \int_{-\infty}^{\infty} dt\, e^{-i\omega t}\,\underline{\tilde{\chi}(\omega)}$$

$$\tilde{\chi}(\omega) = \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} \frac{d\omega_1}{2\pi} \int_{-\infty}^{\infty} \frac{d\omega_2}{2\pi}\, S_R(\omega, \tau_2, \tau_1)\, e^{-i(\omega_1 - \omega_2)\tau_2 - i\omega_1 \tau_1}$$

$$\times \int_{-\infty}^{\infty} d\tau_2'\, E^{(+)}(\tau_2')\, e^{i\omega_2 \tau_2'} \int_{-\infty}^{\infty} d\tau_1'\, E^{(-)}(\tau_1')\, e^{-i\omega_1 \tau_1'}$$

$$+ \ldots$$

$$= \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\infty} d\tau_1 \int_{-\infty}^{\infty} d\tau_1' \int_{-\infty}^{\infty} d\tau_2'\, S_R(\omega, \tau_2, \tau_1)\, \delta(\tau_2 + \tau_2')\, \delta(\tau_2 + \tau_1 + \tau_1')$$

$$\times E^{(+)}(\tau_2')\, E^{(-)}(\tau_1')$$

$$+ \ldots$$

$$= \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\infty} d\tau_1\, S_R(\omega, \tau_2, \tau_1)\, E^{(+)}(\underset{t-\tau_1}{-\tau_2})\, E^{(-)}(\underset{t-\tau_3}{-\tau_2 - \tau_1})$$

$$+ \int_{-\infty}^{\infty} d\tau_2 \int_{-\infty}^{\infty} d\tau_1\, S_{NR}(\omega, \tau_2, \tau_1)\, E^{(-)}(\underset{t-\tau_1}{-\tau_2})\, E^{(+)}(\underset{t-\tau_3}{-\tau_2 - \tau_1})$$

$t - \tau_3 \approx 0 \Leftarrow$ probe pulse is infitely short

we detect:

$$\mathrm{Re}\; i\tilde{\chi}(\omega) e^{i\phi} = -\mathrm{Im}\, \tilde{\chi}(\omega) e^{i\phi} = -\mathrm{Im}\left(\overset{-i}{(i)^3} \sum_\varepsilon R_\varepsilon \right) e^{i\phi}$$

$$= \boxed{\mathrm{Re} \sum_\varepsilon R_\varepsilon\, e^{i\phi}}$$

we detect Liouville pathways up to the phase factor.

Let us consider $\phi = 0$; what can we achieve with this?

rephasing pathways

$$R(t,T,\tau) \approx \langle d^4 \rangle \, \mathcal{U}_{mgmg}(t)\, \mathcal{U}(T)\, \mathcal{U}_{gngn}(\tau)$$

we detect

$$\mathrm{Re}\, R(\omega,T,\tau) \simeq \langle d^4 \rangle \, \mathrm{Re} \underbrace{\int_0^\infty dt\, \mathcal{U}_{mgmg}(t)\, e^{i\omega t}}_{G_{mg}(\omega)} \mathcal{U}(T)\, \mathcal{U}_{gngn}(\tau)$$

$G_{mg}(\omega)$ ← complex lineshape

If $T = \tau = 0$

$$\mathrm{Re}\, R(\omega,0,0) \approx \langle d^4 \rangle \, \mathrm{Re}\, G_{mg}(\omega)$$

↑ absorption lineshape $\alpha(\omega)$

$$\int_0^\infty d\tau\, \mathcal{U}_{gngn}(\tau)\, e^{-i\omega_\tau \tau} = G^*_{mg}(\omega_\tau)$$

what if we can detect complex signals

$$R_R(\omega,T,\omega_\tau) = \int_{-\infty}^{\infty} d\tau \, \overset{\theta(\tau)}{R_R}(\omega,T,\tau)\, e^{-i\omega_\tau \tau} \approx \langle d^4 \rangle \, G_{mg}(\omega)\, \mathcal{U}(T)\, G^*_{mg}(\omega_\tau)$$

$$R_{NR}(\omega,T,\omega_\tau) = \int_{-\infty}^{\infty} d\tau\, R_{NR}(\omega,T,\tau)\, e^{i\omega_\tau \tau} \approx \langle d^4 \rangle \, G_{mg}(\omega)\, \mathcal{U}(T)\, G_{mg}(\omega_\tau)$$

Combining rephasing and non-rephasing signals

$$R_R(\omega,T,\omega_\tau) + R_{NR}(\omega,T,\omega_\tau) \approx \langle d^4\rangle G_{mg}(\omega)\,\mathcal{U}(T)\,\underbrace{\mathrm{Re}\,G_{mg}(\omega_\tau)}_{\alpha_m(\omega_\tau)}$$

$$\mathrm{Re}\left\{R_R(\omega,T,\omega_\tau) + R_{NR}(\omega,T,\omega_\tau)\right\} \approx \langle d^4\rangle \underbrace{\mathrm{Re}\,G_{mg}(\omega)}_{\alpha_m(\omega)}\,\underline{\mathcal{U}(T)}\,\alpha(\omega_\tau)$$

We can detect absorption spectra of different transitions „connected" by evolution of excited state populations!

Complex rephasing signal

order of pulses

$\tau > 0$ $\qquad S_R(\omega_t, T, \tau)$ $\qquad$ 1 − 2 − 3

Complex non-rephasing signal

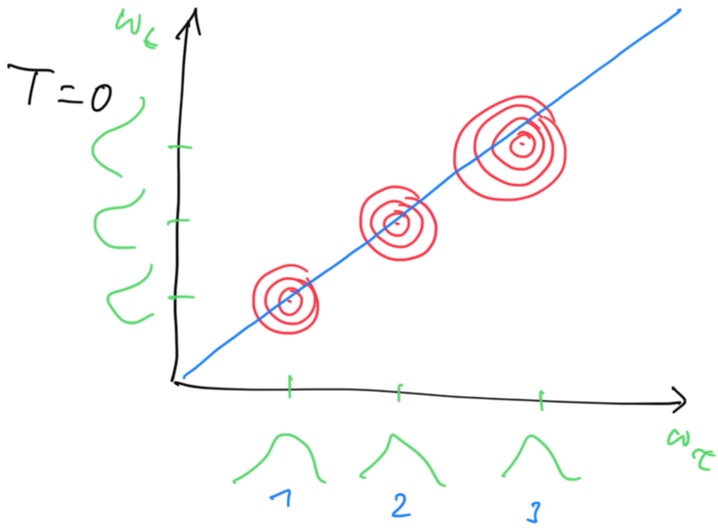
$\tau < 0$ $\qquad S_{NR}(\omega_t, T, \tau)$ $\qquad$ 2 − 1 − 3

2D coherent spectrum

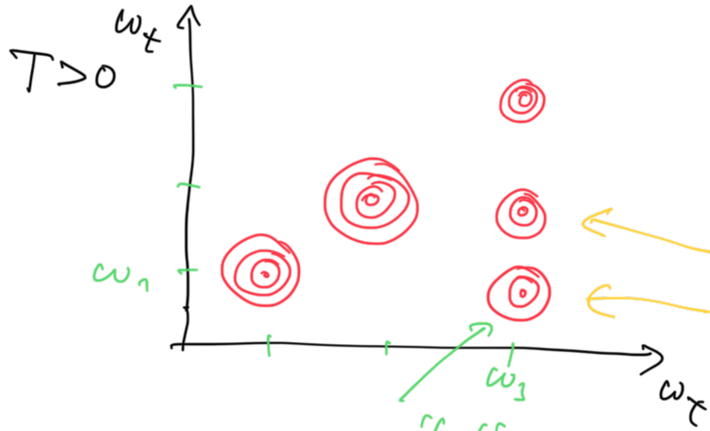
$$\boxed{\tilde{S}(\omega_t, T, \omega_\tau) = \int_0^\infty d\tau\, S_R(\omega_t, T, \tau)\, e^{-i\omega_\tau \tau} + \int_0^\infty d|\tau|\, S_{NR}(\omega_t, T, |\tau|)\, e^{i\omega_\tau|\tau|}}$$

$$\simeq \sum_{\substack{mn \\ kl}} \langle d_k d_l d_m d_n \rangle_\Omega \, \alpha_k(\omega_t) \, \mathcal{U}_{kl\,mn}(T) \, \alpha_m(\omega_\tau)$$

$$\approx \sum_{\substack{m \\ k}} \langle d_k^2 d_m^2 \rangle_\Omega \, \alpha_k(\omega_t) \, \mathcal{U}_{kk\,mm}(T) \, \alpha_m(\omega_\tau)$$



$$\mathcal{U}_{kkmm}(T) \approx \delta_{km}$$



$\mathcal{U}_{11\,33}(T) > 0$

$\mathcal{U}_{2233}(T) > 0$

cross-peaks
due to energy transfer

excitation
started at ω_3
and ended up on ω_1

Two conditions

1) complex signals
2) problem of phase ϕ