Geometry of a three-pulse experiment

$\vec{P}(\vec{r},t)$

this depence originates from $\vec{E}$

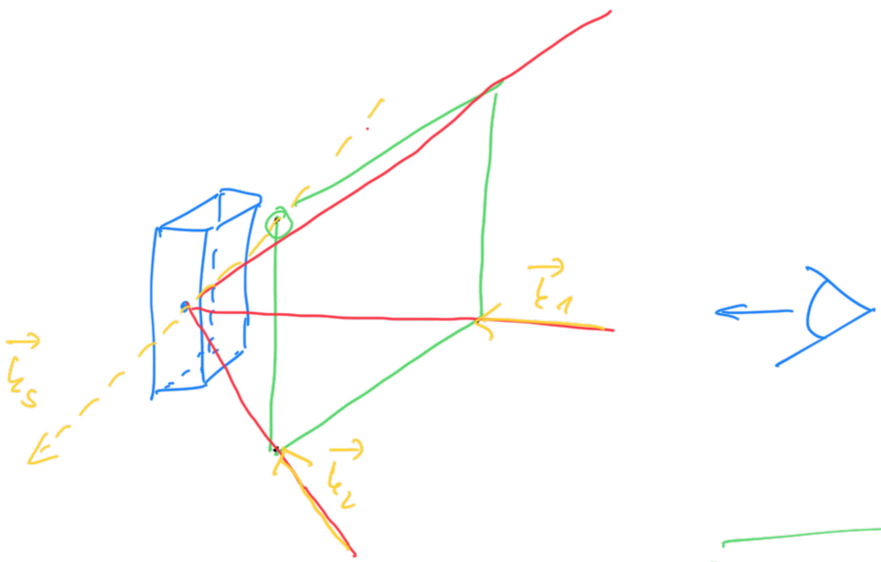
- molecules do not interact with each other

$$E_s(t) \approx i\omega P^{(3)}_{\vec{k}_s}(t)\, \ell$$

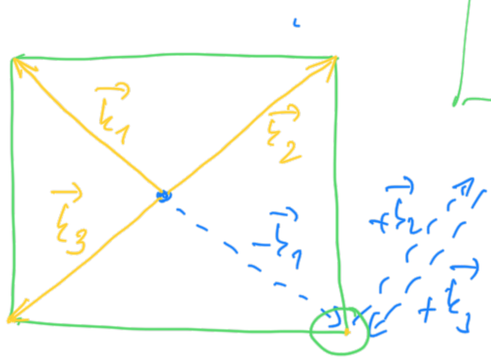
length of the path trough the rample

signal direction

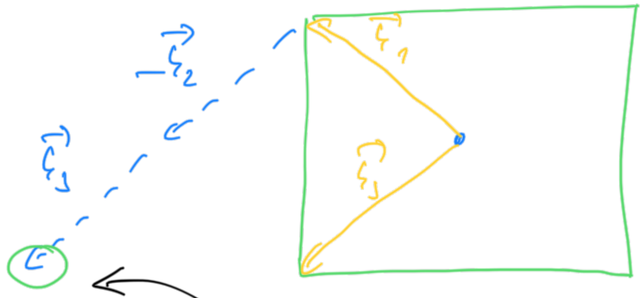
$$\vec{k}_s = \pm\vec{k}_1 \pm \vec{k}_2 \pm \vec{k}_3$$



$$\boxed{\vec{k}_s = -\vec{k}_1 + \vec{k}_2 + \vec{k}_3}$$



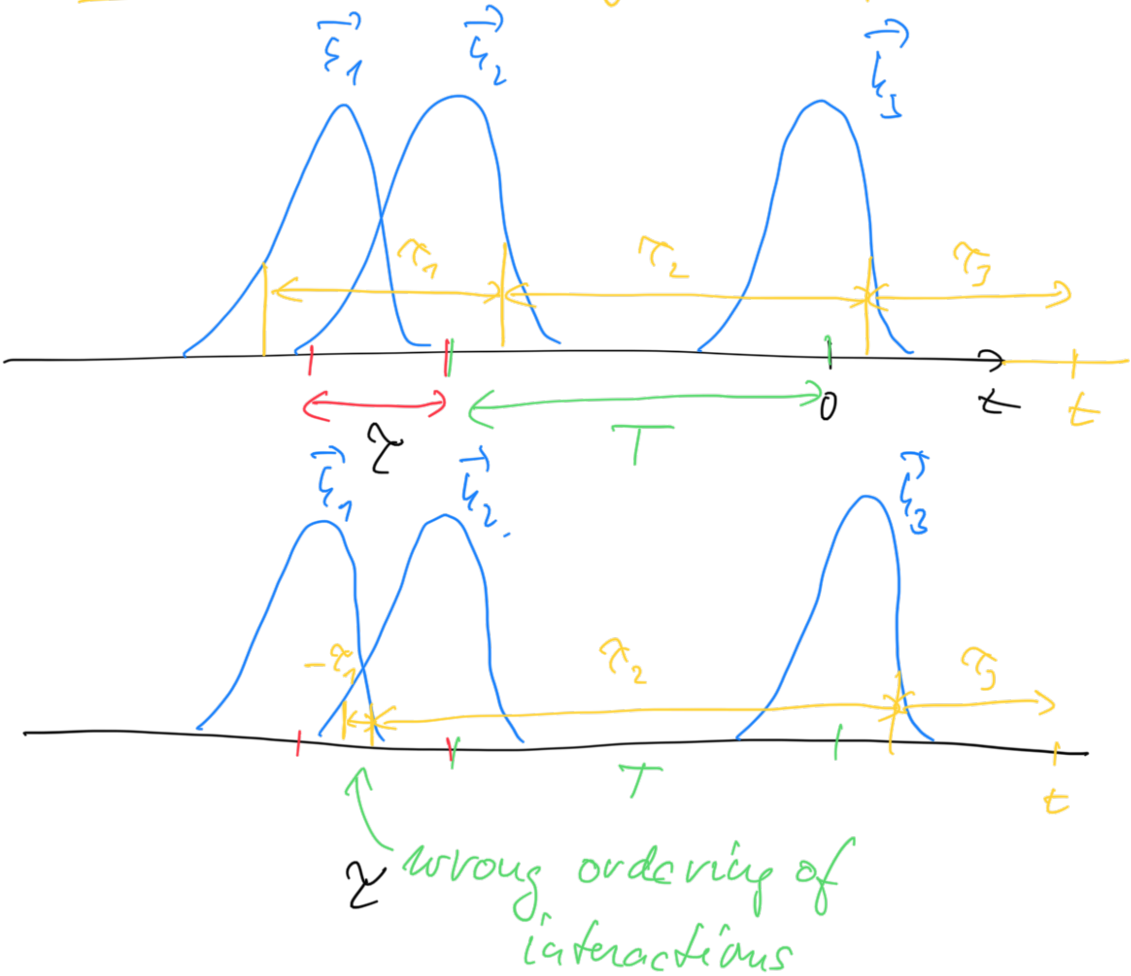
ordering 1-2-3



$$\vec{k}_s = \vec{k}_1 - \vec{k}_2 + \vec{k}_3$$

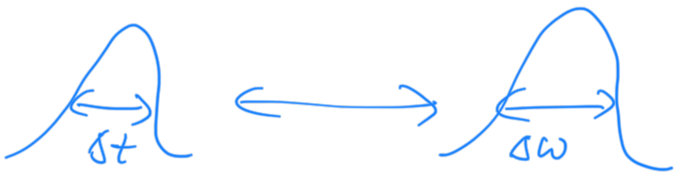
ordering 1–2–3   place to detect non-rephasing signal

Problems with ordering in finite pulses



This problem occurs when spectroscopic technique requires scanning of τ including $\tau \simeq 0$.

Finite pulses

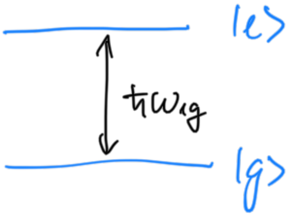


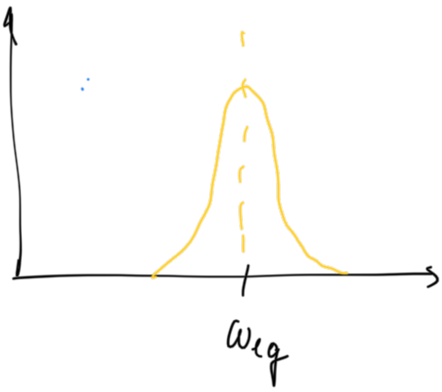
Distortions of the spectrum

- bandwidth problem can be corrected
- pulse ordering problem cannot be corrected

Relation of Liouville pathways to absorption lineshapes

2-level system





$$\alpha(\omega) \approx \frac{\omega}{nc} \chi''(\omega)$$

$\hookleftarrow$ Im $\chi^{(1)}(\omega)$

linear

$$\vec{P}^{(1)}(t,\vec{r}) \rightarrow \vec{P}^{(1)}(t) \xrightarrow{FT} \vec{P}^{(1)}(\omega) = \varepsilon_0 \chi^{(1)}(\omega) \underline{\vec{E}(\omega)}$$

time domain

$$\vec{P}^{(1)}(t) = \varepsilon_0 \int_0^\infty d\tau \, S^{(1)}(\tau)\vec{E}(t-\tau)$$

First order response function

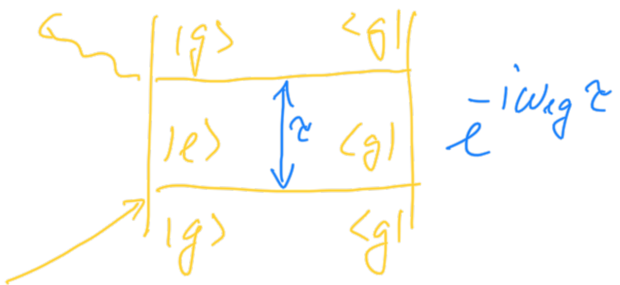
$$S^{(1)}(t) = \frac{i}{\hbar} tr\{\hat{\vec{\mu}}\, \mathcal{U}_0(\tau)\, \mathcal{V}\, \hat{\rho}(-\infty)\}$$

$$= \frac{i}{\hbar} tr\{\hat{\vec{\mu}}\, \mathcal{U}_0(\tau)[\hat{\vec{\mu}}\hat{\rho}(-\infty) - \hat{\rho}(-\infty)\hat{\vec{\mu}}]\}$$

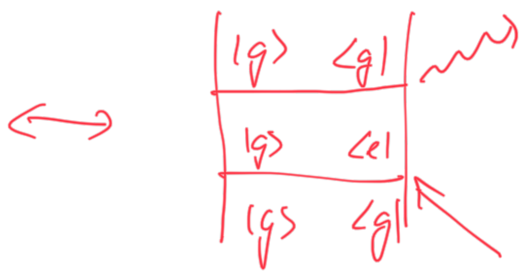
$$= \frac{i}{\hbar} d^2 \Big(tr\{m\, \mathcal{U}_0(\tau)\, m \hat{\rho}(-\infty)\} - tr\{m\, \mathcal{U}_0(\tau)(\hat{\rho}(-\infty) m)\} \Big)$$

First order

Liouville pathways



$J_1(\tau)$



$J_1^*(\tau)$

$$\chi''(\omega) = Im \int_{-\infty}^{\infty} d\tau\, S^{(1)}(\tau)\, e^{+i\omega\tau} = Im \int_0^\infty d\tau \left(\frac{i}{\hbar}\right) d^2 \left(J_1(\tau) - J_1^*(\tau)\right) \times e^{i\omega\tau}$$

$$= I_\omega \Big(\int_0^\infty d\tau \, \frac{i}{\hbar} \tilde{J}_1(\tau) \, e^{-i\omega_{eg}\tau} e^{i\omega\tau}$$

$\omega \approx \omega_{eg}$

$$- \underbrace{\int_0^\infty d\tau \, \frac{i}{\hbar} \tilde{J}_1^*(\tau) \, e^{i\omega_{eg}\tau} e^{i\omega\tau}}_{\approx 0} \Big)$$

$$= I_\omega \int_0^\infty d\tau \, \frac{i}{\hbar} J_1(\tau) \, e^{i\omega\tau} = \mathrm{Re} \, \frac{d^2}{\hbar} \int_0^\infty d\tau \, \mathrm{tr}\{ m \, \mathcal{U}_0(\tau) + m \rho(-\infty) \} e^{i\omega\tau}$$

$m = |e\rangle\langle g| + |g\rangle\langle e|$

$$= \frac{d^2}{\hbar} \mathrm{Re} \int_0^\infty d\tau \, \underbrace{\mathcal{U}_{eg\,eg}(\tau) \, e^{i\omega\tau}}$$

$e^{-i\omega_{eg}\tau - \Gamma_{eg}\tau}$

$$= \frac{d^2}{\hbar} \mathrm{Re} \int_0^\infty d\tau \, e^{-i\omega_{eg}\tau - \Gamma_{eg}\tau + i\omega\tau}$$

$$= \frac{d^2}{\hbar} \mathrm{Re} \, \frac{-1}{-i\omega_{eg} - \Gamma_{eg} + i\omega} = \frac{d^2}{\hbar} \mathrm{Re} \, \frac{1}{\Gamma_{eg} - i(\omega_{eg} - \omega)} \cdot \frac{\Gamma_{eg} + i(\omega - \omega_{eg})}{\Gamma_{eg} + i(\omega - \omega_{eg})}$$

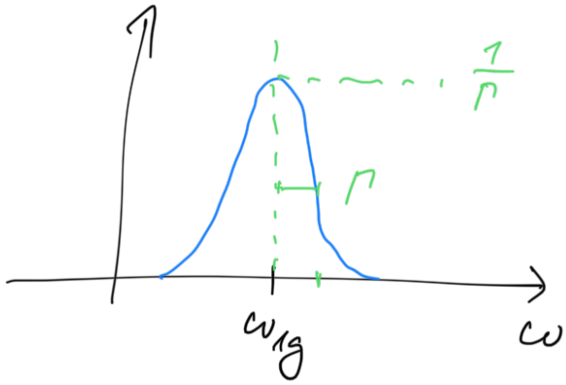
$$= \frac{d^2}{\hbar} \mathrm{Re} \, \frac{\Gamma_{eg} + i(\omega - \omega_{eg})}{\Gamma_{eg}^2 + (\omega - \omega_{eg})^2} = \frac{d^2}{\hbar} \, \frac{\Gamma_{eg}}{\Gamma_{eg}^2 + (\omega - \omega_{eg})^2}$$

Lorentz

Lineshape

$$\chi''(\omega) = \frac{d^2}{\hbar}\tilde{G}(\omega-\omega_{1g})$$

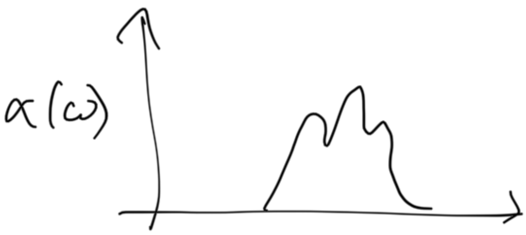
lineshape

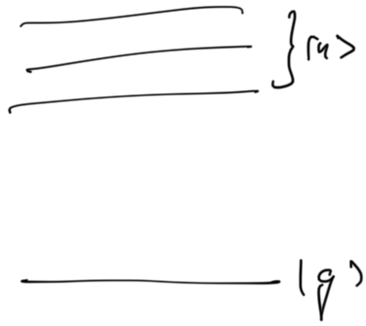


$$\boxed{G_{eg}(\omega) = \int_0^\infty dt\; u_{egeg}(t)\, e^{i\omega t}}$$

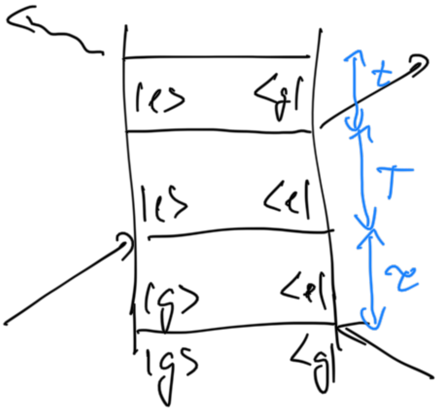
$$\boxed{\tilde{G}(\omega-\omega_{eg}) = \mathrm{Re}\, G(\omega-\omega_{eg})}$$

$$\boxed{\alpha(\omega) \approx \sum_n \mathrm{Re}\, G_{ng}(\omega)}$$





Liouville pathway example



$$R_2(t;T,\tau) \sim E_s(t;T,\tau)$$

$$\sim \mathcal{U}_{egeg}(t)\,\mathcal{U}_{eeee}(T)\,\mathcal{U}_{gege}(\tau)$$

$$\mathcal{U}_{egeg}(t) \xrightarrow{FT} G_{eg}(\omega)$$

$$\mathcal{U}_{gege}(t) \xrightarrow{FT} G^*_{eg}(\omega)$$

$$\boxed{\int_0^\infty dt\, \mathcal{U}_{gngn}(t)\, e^{-i\omega t} = G^*_{ng}(\omega)}$$

$$\mathcal{U}_{gngn}(t) = \mathcal{U}^*_{ngng}(t)$$

Signal field E_s may be detected by heterodyne detection method (background free)

$$E = E_{LO} + E_s$$

local oscillator

We detect $|E(\omega)|^2$

$$E(\omega) = E_{LO}(\omega) + E_s(\omega, T, \tau)$$

$$|E(\omega)|^2 = |E_{LO}(\omega)|^2 + \cancel{|E_s(\omega)|^2} + \underline{2\,\mathrm{Re}\, E_{LO}^*(\omega) E_s(\omega)}$$

small

$$E_{LO}(\omega) = |E_{LO}(\omega)|\, e^{i\phi(\omega)}$$

Detection:
$$\frac{2\,\mathrm{Re}\, E_{LO}^*(\omega) E_s(\omega)}{\sqrt{|E_{LO}(\omega)|^2}} = \underline{2\,\mathrm{Re}\, e^{i\phi(\omega)} E_s(\omega)}$$

Phase of the LO is important

what is the influence of the phase uncertainty on dection of a lineshap?

$E_s(t;T,\tau)$; $T=0$, $\tau=0$

$\mathcal{U}_{eeee}(\tau=0)=1$; $\mathcal{U}_{gege}(\tau=0)=1$

$$E_s(t, T=0, \tau=0) \sim \mathcal{U}_{egeg}(t) \xrightarrow[FT]{} G_{eg}(\omega) \sim E_s(\omega)$$

$$\boxed{\mathrm{Re}\, G_{eg}(\omega) \sim \mathrm{Re}\, E_s(\omega) \sim \alpha(\omega)}$$

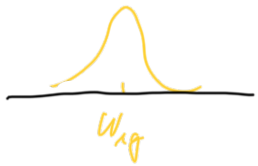
$$\alpha_\phi(\omega) \approx \mathrm{Re}\, e^{i\phi} \int_0^\infty dt\, \mathcal{U}_{egeg}(t)\, e^{i\omega t}$$

$$= \mathrm{Re}\, e^{i\phi} \int_0^\infty dt\, e^{-\Gamma_{eg} t - i\omega_{eg} t}\, e^{i\omega t}$$

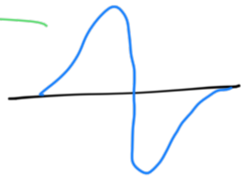
$$= \mathrm{Re}\, e^{i\phi} \frac{\Gamma - i(\omega_{eg}-\omega)}{\Gamma^2 + (\omega_{eg}-\omega)^2}$$

complex Lorentz Lineshape

$\phi = 0 \quad \longrightarrow \quad \dfrac{\mu}{\mu^2 + (\omega_{eg} - \omega)^2}$

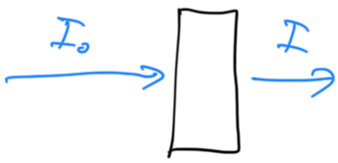


$\phi \neq 0 \quad \longrightarrow \quad \dfrac{\mu \cos\phi + (\omega_{eg} - \omega)\sin\phi}{\mu^2 + (\omega_{eg} - \omega)^2}$



How to detect absorptive lineshapes in heterodyne detection?

Homodyne detection – in linear absorption



$\dfrac{I}{I_0} = e^{-\alpha h}$ ← absorption coefficient (α)

$\Delta I = I - I_0$

$\dfrac{\Delta I}{I} \approx e^{-\alpha h} - 1 \approx -\alpha h$

$$-\nabla^2 \vec{E}(\vec{r},t) + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{E}(\vec{r},t) = -\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{P}^{(1)}(\vec{r},t) \qquad \vec{k}_s \equiv \vec{k}$$

$$\vec{E}(\vec{r},t) = \vec{E}_0(\vec{r},t) + \vec{E}_s(\vec{r},t)$$

$$-\nabla^2 \vec{E}_s(\vec{r},t) + \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{E}_s(\vec{r},t) = -\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\vec{P}^{(1)}(\vec{r},t)$$

$$E_s(t) \sim i\omega \vec{P}^{(1)}(t)\, h$$

$$\vec{E}(\vec{r},t) = \vec{E}_0(\vec{r},t) + \underline{\propto} \, i\omega \vec{P}^{(1)}(t)\, \underline{h}$$

$$I_0 \sim |E_0(\omega)|^2$$

$$I \sim |E_0(\omega)|^2 + \kappa^2 h^2 \omega^2 |P^{(1)}(\omega)|^2 + 2\,\mathrm{Re}\, E_0^*(\omega)\, \kappa i \omega h P(\omega)$$

$$\frac{\Delta I}{I_0} = \frac{I - I_0}{I_0} = \frac{2\,\mathrm{Re}\, E_0^*(\omega)\, \kappa i \omega P(\omega) h}{I_0}$$

$$-\alpha h$$

$\mathrm{Re}\, i(a+ib)$
$= \mathrm{Re}(ia - b)$
$= -b$

$$\alpha(\omega) \approx +\mathrm{Im}\, \frac{\omega E_0^*(\omega) P(\omega)}{I_0}$$

$$\alpha(\omega) \approx \mathrm{Im}\, \frac{\omega E_0^*(\omega)\, \chi(\omega) E_0(\omega)}{I_0}$$

$$\frac{1}{h}\frac{\Delta I}{I} = \boxed{\alpha(\omega) \approx \mathrm{Im}\, \frac{\omega \cancel{E_0^*(\omega)}\, \chi(\omega) \cancel{E_0(\omega)}}{\cancel{E_0^*(\omega)}\, \cancel{E_0(\omega)}} = \omega\, \mathrm{Im}\, \chi(\omega)}$$

There is no problem of phase in absorption experiment!